Methane Dynamics in a Southern Ontario Calcareous Fen

by

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Author's Declaration

This thesis consists of material all of which I authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

This thesis is written in the manuscript format, thus some of the information presented within the manuscript may have been previously stated.

This thesis reports on data that was collected at a Southern Ontario calcareous fen near Guelph, Ontario from the years 2016-2019. Data in 2016 and 2017 were gathered by field assistants working within the Wetland Soils and Greenhouse Gas Exchange lab while field data from 2018 and 2019 was collected and overseen by Ryan Kangro. There is also data that was collected from a greenhouse experiment that was run in 2019 by Ryan Kangro.

Maria Strack assisted in the design, format and structure of data collection as well as funding and manuscript revisions. Contents contained in the manuscript including figures and tables were written in entirety by Ryan Kangro and reviewed by Maria Strack prior to submission.

Abstract

Peatlands are important ecosystems that are pivotal for the global carbon budget. They have the ability to take carbon dioxide out of the atmosphere and store it within peat, which has very slow decomposition rates. Peatlands reduce the rate of organic matter decomposition due to their saturated environments year-round. While these conditions are needed for the storage of carbon, they also result in the production of methane (CH_4). CH_4 emission is an important function of peatlands as it is a highly potent greenhouse gas; therefore, understanding the mechanisms behind this process is crucial.

While CH_4 flux has been studied for several decades in peatlands, several gaps remain due the complex relationships that exist. One of the transportation methods of CH_4 (ebullition) has often been ignored and disregarded, while measurements of CH_4 flux during the non-growing season also remain sparse. Additionally, it is important to further our knowledge of various environmental controls of CH_4 for peatland management practices.

Ebullition was captured and measured over the course of 6 months in 2019 using funnel traps. The traps were placed throughout a calcareous fen peatland in Ontario to view spatiotemporal trends. It was found that ebullition was significantly different on both a spatial and temporal scale. Ebullition was consistently the greatest in the sedge location and lowest in the willow. These differences were likely caused by differences in environmental variables such as water table and pore water CH_4 concentration, as well as peat properties. The willow location had higher bulk density and lower organic matter content, which likely reduced the amount of ebullition. On a temporal scale, ebullition peaked in late July and early August. This likely occurred due to soil temperatures being the warmest during this time period. Consistent decreases in water table and atmospheric pressure were also shown to likely enhance ebullition release. In relation to chamber flux measurements over the same time, ebullition contributed 16.4% of total CH_4 emissions. A greenhouse experiment was also conducted to view the effects that vascular vegetation has on ebullition. Bare, willow, and sedge cores were collected that all contained various amounts of vascular plant coverage. Ebullition was greatest in the bare cores that contained no vascular plant coverage, while ebullition was the least in the sedge cores which contained the greatest amount of biomass of *Carex*. Negative correlations were found between belowground biomass and pore water CH_4 concentration which suggests that the presence of roots can restrict that ability for ebullition to form. While vascular plant coverage was present in the willow cores, the amount of vegetation was much less than the sedge cores and did not appear to limit ebullition in a drastic way. Ebullition from this study has been shown to release a sizable amount of CH_4 that should be accounted for as well as vary on a spatiotemporal scale due to changes and differences in environmental variables and peat properties.

Growing season and non-growing season CH_4 fluxes were collected from 2016-2019 allowing investigation of the importance of various environmental controls (water table, soil temperature, pore water CH_4 concentration and vegetation productivity). Over the course of the growing season, higher water table levels consistently resulted in greater CH_4 fluxes. Additionally, on a monthly scale, CH_4 fluxes were at their greatest when soil temperature was the warmest. This suggests that water table is an ideal predictor for longer temporal scales (growing season) while temperature is more appropriate on smaller temporal scales (monthly). Significant differences in CH_4 fluxes were also found spatially in the growing season of 2019 which suggests that CH_4 fluxes are quite variable on a spatial scale (meters) and this needs to be considered during modeling or when calculating overall carbon sequestration in a peatland.

Despite only having measurements for less than half of the non-growing season, three out of the four years had non-growing season emissions surpass 15% of the growing season emissions (25.7, 7.8, 41.0, 21.9%, 2016-2019, respectively). This 15% of the growing season is an important threshold as it is typically used in replace of missing non-growing season fluxes. Having an abnormally high growing season CH_4 emission does not necessarily result in an abnormally high non-growing season. This suggests that relationships between the growing season and non-growing season might be nonexistent. Non-growing season CH_4 fluxes may be more accurately presented by mean measurements rather than a percentage of the growing season.

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Chapter 1: Introduction

Wetlands are ecosystems that contains shallow water or saturated conditions for extended periods of time leading to an influence on vegetation growth (Craft, 2015). They represent an integral ecosystem to the global carbon cycle as they have the ability to pull carbon dioxide (CO_2) out of the atmosphere and trap it below the surface in the form of peat (Gorham, 1991). What allows wetlands to be able to accomplish this is the fact that their inputs of organic matter will typically exceed decomposition rates. As a wetland accumulates more peat over time, it can shift into being classified as a peatland. In Canada, a peatland is defined as a wetland that has accumulated 40 cm of peat or more (Warner and Rubec, 1997). The main contributing factor that allows wetlands and peatlands to be exceptional sinks of CO_2 and have such low decomposition rates is that they typically have a water table near the surface or saturated conditions for long periods of time (Craft, 2015). While these saturated conditions are ideal for carbon sequestration, they are also ideal for the production of methane (CH_4), for which wetlands are the world's largest natural source (Forster et al., 2007). This can be of concern, as when viewed on a 100-year time scale, CH_4 has been reported to be 28 times more effective at trapping heat within the atmosphere compared to CO_2 (Stocker et al., 2013). Due to this, it is important to understand the processes that control wetland and peatland CH_4 emissions, not only for carbon budget and wetland management purposes, but also to inform models that can be used to estimate how wetland CH_4 emissions may change due to ongoing climate change. Modeling wetlands remains a difficult task, however, as they are heterogenous ecosystems that have layers of complex relationships that are often interwoven and influence CH_4 emissions to varying degrees. This can easily be seen when modelling and predicting global CH_4 emissions from wetlands, as studies have typically resulted in a wide range of potential values. In 2007, Menon et al., predicted that on a global scale, wetlands emit 100-231 Tg yr^{-1} of CH_4, while Meng et al. (2012) estimated that a larger value of 256 Tg yr^{-1} of CH_4 is emitted annually. Uncertainties exist and will continue to exist due to the volatile nature of wetlands as well as the fact that our understanding of the mechanisms that drive CH_4 emissions at an ecosystem scale remains incomplete. It is important to further our understanding of the dynamics of this potent greenhouse gas and identify key trends and controls for wetland management practices.

In Canada, there are five different types of wetlands according to the Canadian Wetland Classification System. Shallow water wetlands have lightly flowing or standing water that is less than 2 m in summer with reasonably stable water table levels throughout the year (Warner and Rubec, 1997). Swamps typically have periodically standing water that is fed by nutrient rich groundwater and are made

up of several woody plants such as trees and shrubs (Warner and Rubec, 1997). Marshes consist of slow-moving or persistent standing water that is often alkaline and nutrient rich and are dominated by grass-like species (Warner and Rubec, 1997). Bogs are ombrotrophic ecosystems exhibited in low nutrient and acidic conditions that are a result of only receiving water through precipitation (Warner and Rubec, 1997). Due to these conditions, mosses such as *Sphagnum* typically dominate the vegetation that is present. Finally, fens are wetlands that are sometimes nutrient rich due to their consistent supply of ground water. These nutrient rich waters allow graminoid species to thrive with the addition of some brown mosses (Craft, 2015).

Under saturated conditions, CH_4 is produced from a group of microorganisms called methanogens that contribute to anaerobic decomposition of organic matter (Lai, 2009). As these microorganisms struggle to survive with the presence of oxygen, this makes zones of saturation in the peat critical for the production of CH_4 (Bridgham et al., 2013). Once CH_4 has been produced, it has three possible transportation pathways to reach the atmosphere: diffusion through the peat matrix, plant-mediated transport, and ebullition. Diffusion is a process that occurs throughout wetlands when CH_4 that is produced in the saturated layers of the peat slowly moves along a concentration gradient upwards into potential unsaturated layers and finally into the atmosphere (Walter and Heinmann, 2000). This is an important process as when CH_4 is travelling through unsaturated zones of the peat, methanotrophs, which are another type of microorganism, can consume CH_4 as they produce energy by consuming single-carbon compounds (Hanson and Hanson, 1996). This occurs as present in the unsaturated zones is oxygen, which can be used to oxidize CH_4 into CO_2 (Whalen, 2005) playing an influential role in the overall reduction of CH_4 emissions. Over time, plants present in wetland ecosystems have developed ventilation systems called aerenchyma to help supply their roots, or other areas of their plant structure that are submerged in the anoxic zone, with oxygen (Joabsson et al., 1999). While these ventilation systems are great for transporting oxygen, they also act as a conduit for transporting CH_4, which is abundant in the anoxic zone, to the atmosphere (Strack et al., 2006). Additionally, CH_4 that is being transported through this aerenchyma can bypass potential oxidation that occurs throughout the oxic zone of peat (Van den Pool-van Dasselaar et al., 1999; Whalen, 2005). On the contrary, this aerenchyma can supply the rhizosphere with additional oxygen which could promote oxidation. The final way that CH_4 can reach the atmosphere from the peat is ebullition. Ebullition is the release of bubbles containing CH_4 to the atmosphere, typically from deep layers of the peat. These bubbles are formed when there is a presence of a high concentration of CH_4 (Joyce and Jewell, 2003) and hydrostatic pressure is less than the partial pressure of the dissolved gas (Chanton and Whiting,

1995). Research has shown that changing atmospheric pressure (Tokida et al., 2007) can cause ebullition events to occur, as well as shifts in the water table due to a change in hydrostatic pressure (Price, 2003). Our overall knowledge on ebullition, however, is lacking due to its erratic and unpredictable nature. At times, calculations for annual CH_4 emissions can exclude ebullition, which could result in severely underestimating total emissions.

The amount of CH_4 that a wetland emits is based upon the amount of production and consumption that occurs within it. Each of these processes are influenced by various environmental factors such as water table level, soil temperature and vegetation productivity and therefore vary in space and time (Turetsky et al., 2014). Water table level has the ability to determine the size of both the anoxic and oxic zones of wetlands, which regulates how much CH_4 is produced as well as consumed based on the presence of methanogens and methanotrophs, as well as oxygen (Moore and Knowles, 1989; Moore and Roulet, 1993). Not only can water table levels differ long term, it is also possible to see them vary on a much smaller scale such as week to week. Over a two-year period, Turetsky et al. (2008) observed that CH_4 emissions were much greater in a wet year when compared to a much drier year and even saw differences between sites during the same year due to water table level fluctuations. Additionally, soil temperature can influence CH_4 production (Updegraff et al., 1995) as the activity of microbes will vary depending on temperature (Lai, 2009). More highly active microbes will result in more CH_4 being produced, which occurs in warmer peat (Dunfield et al., 1993). However, this relationship between CH_4 production and temperature can be dependent on water table levels as oxidation is also temperature sensitive (Munir and Strack, 2014). Microforms that are relatively drier (hummocks) can see a decrease in CH_4 emissions during a temperature increase while the opposite is likely to occur in microforms with wetter conditions (hollows) (Munir and Strack, 2014). The productivity of plants can also influence CH_4 emissions by providing additional labile substrates into the peat that are used in the production of CH_4 (Whiting and Chanton, 1992). While all three of these variables have been shown to influence CH_4 emissions in some way, they change on both temporal and spatial scales making CH_4 emissions more difficult to estimate and model (Dise, 1993). It remains important to identify major environmental controls on CH_4 emissions and its components within wetlands, as well as see how these controls might vary amongst past studies from other wetlands.

One major research gap that remains in the study of CH_4 dynamics in wetlands is non-growing season emissions. Many wetlands reside in areas of the world that can experience harsh non-growing seasons making it difficult to measure these emissions. A common practice used to overcome this is to

assume that the non-growing season emissions are equal to 15% of either the growing season (Webster el al., 2018) or annual emissions (Saarnio et al., 2007). However, as discussed previously, environmental variables such as water table level, temperature and plant productivity can influence CH_4 emissions but their relationships in the non-growing season are severely understudied. Even though people tend to assume that the non-growing season is only 15% of the growing season, it is possible that no relationship exists between these two completely different seasons (Treat et al., 2018).

While research has examined various environmental controls of ebullition in waterbodies or wetlands such as marshes and shallow open water areas, ebullition research in more typical peatland systems such as fens is less common. These studies are few and far between and large uncertainties remain. For example, there have been conflicting results on whether the presence of vascular vegetation limits or contributes towards ebullition (Green and Baird, 2012). Similarly, very few studies have been completed comparing non-growing season and growing season CH_4 emissions within Canada, particularly in temperate regions. It is important to further our understanding on how CH_4 emissions may differ in the non-growing season compared to the growing season as it can contribute a significant amount of CH_4 emissions, and also due to the fact that winters will likely be more affected by climate change than the growing season (Treat et al., 2018). Additionally, viewing CH_4 emissions on a multi-year scale can help identify environmental variables that are considered to be major controls. Research addressing these concerns took place within a calcareous fen in southern Ontario. This work being undertaken in a calcareous peatland fen is particularly important for several different reasons. Calcareous fens are a rare type of fen that are nutrient rich, similar to rich fens, with a range of pH from 6.8 to 7.8 (Bedford and Godwin, 2003). They also have greater vascular vegetation species richness compared to other wetland types and are often the home of rare regional plant species (Duval and Waddington, 2018). This makes calcareous fens ideal conservation and restoration landscapes; thus, it is important to gain a greater understanding as to how they function. In addition, calcareous fens are very similar to rich fens in terms of overall environments, so findings from this calcareous fen can improve understand of CH_4 cycling in rich fens in general.

1.1 Objectives

Gaining a greater understanding of ebullition dynamics in more typical peatland systems such as fens will help improve our overall understanding of carbon cycling, which can be used for modelling as well as peatland management practices and restoration. Additionally, studying interannual CH_4 emissions for both the growing and non-growing season will help identify ongoing trends as well as

strong drivers of CH_4 emissions. This study will also provide the opportunity to determine if there appears to be any clear relationships between growing season and non-growing season CH_4 emissions on a year to year basis.

The objectives of this research were to:

1. Quantify ebullition concentration and volume within a southern Ontario calcareous fen and determine spatial (i.e., sampling locations) and temporal (i.e., months) variability.
2. Identify how different types of vascular vegetation and their presence influence the amount of ebullition and its contribution towards total CH_4 emission.
3. Quantify CH_4 emissions in both the growing season and non-growing season across a four-year period (2016-2019) to determine if any relationships exist between the seasons.
4. Identify major environmental controls (e.g., water table, temperature, vegetation type) of CH_4 fluxes on various spatiotemporal scales (e.g., years, months, and sampling locations).

1.2 Study Site

Research was performed within a natural calcareous fen peatland located approximately 20 km south of Guelph, Ontario, Canada. The fen itself is found within Fletcher Creek Ecological Preserve (43°24'55.422" N, 80°7'0.3612" W), which is part of the headwater catchment of Spencer Creek Watershed (Duval and Waddington, 2011). Fletcher Creek, which is a stream that flows through this calcareous fen, has its source near the centre of the catchment as a series of groundwater seeps (Duval et al., 2012). The entire fen has a slight slope of only 30 cm change in elevation over 450 m of stream length (Duval et al., 2012). Due to this slope, a small pool of water has developed in the southernmost portion of the fen that has an abundance of calcite precipitate also known as a marl flat (Miner and Keterling, 2003). Water inputs for this fen in particular are heavily dominated by a groundwater-fed stream that emerges ~400 m northwest of the fen margin (Duval and Waddington, 2018). The adjacent areas of this fen are surrounded by cedar forest. Located approximately 50 m north is an active railroad while a country road runs along the area 150 m to the west and 200 m to the south. Land use outside of the ecological preserve is typically rural homes and agricultural fields. Overall, this fen is dominated by various *Carex* and other sedge species with some shrubs throughout. Across a 30-year average (1981-2010), this area receives approximately 916.5 mm of precipitation a year with an annual daily average temperature of 7.0 °C (Government of Canada, 2019).

In 2016, six metal collars (60 cm x 60 cm) were inserted ~15-25 cm into the peat and were used to capture greenhouse gas exchange measurements at specific locations. Three collars (FL1-3) were installed ~20 m north of the pooling area (referred to as 'sedge' grouping), while an additional three (FL4-6) more were installed ~ 15m east of those collars near a small tributary stream (referred to as 'stream' grouping). In 2017, one additional collar was added to each of these locations to improve spatial representation within each zone (FL0, FL7). In April 2019, four new collars (FL8-FL11) were introduced in the fen and consisted of a mix of *Carex* spp. as well as *Salix* spp. (willow) to determine if *Salix* has a different effect on greenhouse gas exchange compared to *Carex,* which heavily dominates the other two groups of collars. These collars (referred to as 'willow' grouping) were installed ~8 m north of the group of stream collars. Funnel traps were also installed throughout these locations in the summer of 2019 to quantify ebullition. Nine peat cores were extracted from this area for a greenhouse experiment. These nine cores were separated into three different types: bare, sedge and willow. The bare cores were taken either from the small tributary stream or on its edge where vascular plants were not present. Sedge cores were collected in the area northeast of the willow collars, while the willow cores were collected in the open area north of the sedge collars (Figure 1.1).

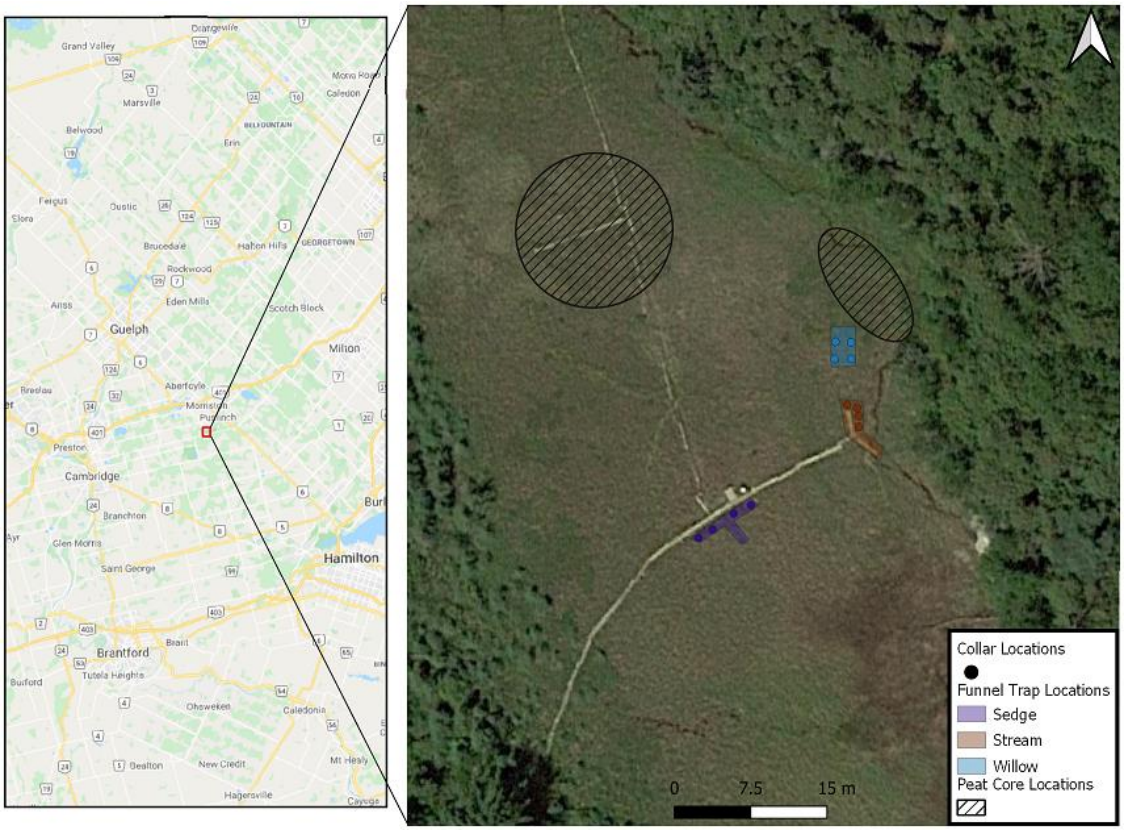

Figure 1.1: Study site map displaying locations of collars, funnel traps, and core collection.

Three additional chapters are found within this thesis that address various research topics on CH_4 dynamics in a calcareous fen. Chapter 2 focused on the study of ebullition over the course of one growing season. This chapter aimed to determine spatiotemporal trends of ebullition that exist within the fen. Environmental controls were also to be examined to determine which ones were a major control of ebullition. Finally, this chapter also contains a greenhouse experiment that was done to assess the effect that vascular vegetation has on ebullition. Chapter 3 focused on examining CH_4 fluxes over a four-year period. Long term trends and controls of fluxes were investigated, as well as how fluxes vary throughout the fen. Additionally, non-growing season CH_4 fluxes were assessed to determine if any relationships exist between the two differing seasons. Lastly, Chapter 4 provides a summary of the major findings from each chapter, limitations of the present study, and suggests future research ideas.

Chapter 2: Quantifying Seasonal Trends and Controls of Ebullition in a Southern Ontario Calcareous Fen

2.1 Introduction

A peatland's potential for global warming or cooling is highly dependent on the amount of methane (CH_4) that is released into the atmosphere. Estimating peatland CH_4 emissions remains a difficult task, however, due to the complex makeup and interwoven interactions that can lead to extensive spatial and temporal variation (Limpens et al., 2008). Emission rates will vary throughout a peatland due to differences in production and consumption of CH_4. These are bound to vary within a peatland due to differences in environmental variables that act as controls on CH_4 cycling such as soil temperature, plant productivity and water table level (Turetsky et al., 2014). Peat temperature can influence CH_4 emissions as temperature influences the activity of methanogens, which are CH_4 producing microorganism (Lai, 2009), while plant productivity can provide additional labile substrates which are used in the production of CH_4 (Whiting and Chanton, 1992). Water table levels influence the number of available methanogens, methanotrophs, which are microorganisms that consumes CH_4, as well as how much oxygen is present in the peat by controlling the size of anoxic and oxic zones (Moore and Roulet, 1993). CH_4 is transported from the peat to the atmosphere through three major pathways, which are diffusion, plant-mediated transport, and ebullition. However, a lack of research remains for ebullition due to the difficulties that come with trying to capture and quantify this process (Green and Baird, 2012; Ramirez et al., 2017). This study aims to gain a greater understanding of this process by quantifying ebullition in a temperate calcareous fen peatland over the course of one growing season and to investigate various controls on its magnitude.

Ebullition is the release of bubbles that contain CH_4 into the atmosphere (Coulthard et al., 2009). It can further be broken down into steady and episodic ebullition. Steady ebullition occurs when there is a consistent release of bubbles that contain CH_4 that move up through the peat to the surface where they are released into the atmosphere (Green and Baird, 2012). However, while moving through the oxic zone, it is possible that these bubbles can be consumed completely or partially by methanotrophs (Green and Baird, 2012). These bubbles can also be released in a large number and/or volume over a short (minutes) or longer (hours) time frame. Episodic ebullition will typically occur when groups of bubbles or sometimes one large bubble containing high concentrations of CH_4 travels up through the water table and into the atmosphere (Green and Baird, 2012). Due to the physical size as well as the amount of CH_4 within them, these bubbles are typically able to bypass methanotrophs and

avoid consumption (Rosenberry et al., 2006). The result of this is that fluxes during episodic ebullition will typically be greater with more variability than steady ebullition. These trapped bubbles have also been revealed to be released due to decreases in atmospheric pressure as it can influence the buoyancy that is keeping them in place (Tokida et al., 2007).

Research has shown that ebullition can vary throughout the year with it sometimes peaking during the summer months (Goodrich et al., 2011). This is likely due to the fact that during summer months, there are typically higher temperatures that result in higher rates of CH_4 production, as well as reduced solubility of CH_4 (Goodrich et al., 2011) leading to its shift from an aqueous to gaseous state (Strack et al., 2005). However, the ebullition peak can still vary based on the year, or possibly the geographical location of the peatland. For instance, Goodrich et al. (2011) studied a fen located in New Hampshire, USA and reported an ebullition peak in mid-August. Meanwhile, in Norfolk Broads UK, Stanley et al. (2019) found that ebullition peaked in both May and June rather than mid-August in two different fens. These discrepancies could indicate that ebullition functions differently depending on geographical location due to differences in climate, the individual peatland soil and vegetation composition, or possibly due to the fact that measurements were taken in different years. Additionally, there remains a lack of research exploring how ebullition varies spatially within one single peatland. Due to changes in vegetation, water table levels, peat properties such as bulk density, and available subsurface CH_4 pools, it is likely that ebullition rates are not consistent throughout a single peatland. While Stanley et al. (2019) discovered that environmental variables such as water level and soil temperature were important factors for ebullition flux, it is essential to determine if similar relationships exist in other peatlands.

Another important variable that can likely influence the amount of ebullition is the type of vegetation cover that is present in the peatland. The presence of certain species of vascular plants has been shown to reduce the amount of ebullition as they can transport CH_4 that is found deep in the peat into the atmosphere through their aerenchyma which can subsequently deplete pore water concentrations of CH_4 (Chanton, 2005). Furthermore, aerenchyma have been shown to enhance CH_4 oxidation in the rhizosphere, which can further deplete CH_4 concentrations (Chanton, 2005). When this occurs, there may not be enough available CH_4 to exceed solubility under local conditions and thus bubbles will not form and ebullition, not occur. While a few studies have been completed to investigate the effect of vegetation on ebullition, conflicting results remain. In 1998, Frenzel and Rudolph observed an area of bubbles within the peat profile that were located close to a dense network of roots but state

that the roots could possibly block and trap bubbles that are produced deeper in the peat profiles. Christensen et al. (2003) found that when sedges were 'very dense' that ebullition contributed up to 50% of the total CH_4 fluxes. Meanwhile, Ström et al. (2005) compared the ebullition flux between *Carex*, *Eriophorum*, and *Juncus* and observed that ebullition had the greatest contribution to overall CH_4 emissions in *Carex* with 23.4%. *Eriophorum* had only 3.5% of their CH_4 emissions come from ebullition while *Juncus* ebullition was undetectable. In contrast, Green and Baird (2012) found that their sedge samples only had ebullition contribute 7% to the total CH_4 emissions while their no-sedge samples contributed on average 28%, but that the total mass of CH_4 released by ebullition was similar in both treatments. Based on these findings, it is apparent that the influence of vascular plants on ebullition within peatlands remains uncertain and is likely species specific.

Several unknowns of ebullition remain in peatland environments. To address this lack of clarity, ebullition was quantified throughout three locations in a southern Ontario fen. The objectives of this chapter are to: (1) identify temporal (months) and spatial (location) patterns of ebullition and (2) determine how various environmental factors (water table, soil temperature, pore water CH_4 concentration, precipitation and atmospheric pressure) influence ebullition. It is hypothesized that ebullition will have an increasing trend throughout the summer that differs amongst locations and that certain environmental factors such as temperature and water table will enhance ebullition as they increase. Furthermore, a greenhouse experiment was designed to test an additional objective, (3) the effect that vascular plant type and presence have on ebullition frequency, concentration and its contribution towards overall CH_4 emissions. It was expected that increased vascular plant cover would reduce the amount of ebullition present due to a reduced amount of subsurface CH_4.

2.2 Methods

2.2.1 Study Site

This study took place in a calcareous fen located in southern Ontario in the township of Puslinch, ~20 km south of Guelph. It is located within Fletcher Creek Ecological Preserve (43°24'55.422" N, 80°7'0.3612" W) which falls within the Spencer Creek Watershed. The majority of the fen is dominated by various sedge species, specifically *Carex* spp. with shrubs located throughout. A cedar forest covers the surrounding area of the fen, while landcover outside of the ecological preserve are rural homes and farmland. Over a 30-year period (1981-2010), the average daily annual temperature for this region is 7.0 °C while receiving approximately 916.5 mm of precipitation yearly (Government of Canada, 2019). Peat was 60 to 80 cm thick across the sampling areas.

Nine funnel traps (27 total) were installed in three different areas in the fen to measure ebullition (Figure 1.1). The first area was a central location in the fen that is dominated by *Carex* spp. including *Carex aqualitis* and *Carex livida* (referred to as 'sedge'). The second location was near a tributary stream closer to the edge of the fen which was also fairly dominated by *Carex* spp. (referred to as 'stream'). Finally, at the last location was an area of the fen that was dominated by a mix of both *Salix* spp. and *Carex* spp. (referred to as 'willow').

A total of nine peat cores (20 cm inner diameter, 45 cm in length) from three different vascular vegetation types were also extracted from this fen. The first type of peat core that was collected was bare. This meant that these peat cores consisted of bare peat, with no vascular vegetation present. The next type of peat cores that were collected consisted of *Salix* spp. with a sparse amount of *Carex* spp. (referred to as 'willow'). The final type of peat cores that were sampled from the fen were strictly dominated by *Carex* spp. (referred to as 'sedge'). While *Carex* was present in two of the different vegetation types, it was much more dominant and thrived more in the 'sedge' cores compared to the 'willow'.

2.2.2 Funnel Traps

Handmade gas traps were used to measure ebullition amounts throughout the year 2019 (Strack and Waddington, 2008). These traps were made by taking plastic funnels (15.2 cm diameter) and inverting them so that the spout was pointing upwards and then a syringe with a three-way stopcock was sealed onto plastic tubing (2 cm inner diameter) that was attached to the spout of the funnel using a silicone adhesive. In total, 27 traps were made. Nine traps were placed in each of the three specified areas of the fen. To install these traps, peat was carefully cut and removed with a breadknife and one trap was placed within each hole slightly below the surface, but in contact with the water table, and then covered with the peat that was previously removed. Once in place, water was pulled up into the syringe that was attached to each funnel. If ebullition were to occur, the gas bubbles would rise to the top of each syringe, displacing the water that was once there. Once this occurred, measurements of how much gas accumulated in each syringe was recorded. The gas traps were installed on May 15th, 2019 and were recorded until October 25th, 2019. Recordings of how much ebullition had occurred was done on a weekly basis. Throughout sampling, at times some funnels were unable to have their volume of ebullition recorded due to fluctuations in the water table that would cause the water table to briefly drop below depths where the funnels were not buried. This occurred more often in the willow area as

several traps were placed near a large *Salix* bush which likely caused the water table to drop more frequently due to a greater need for water.

2.2.3 Gas Concentration in Traps

To determine how much CH_4 was being released into the atmosphere through ebullition, the gas that was present in the funnel traps was extracted and stored in a 12 mL pre-evacuated vial (Exetainer, Labco Ltd., UK) roughly every other week. Vials were overpressured with 20 mL of gas. If ebullition amounts were less than 20 mL, ambient air was added to each sample to ensure that each exetainer had equal volume. Samples of ambient air were also collected. These samples were then analyzed on a gas chromatograph (GC; Shimadzu GC2014) with a flame ionization detector to determine CH_4 concentrations. Afterwards, true ebullition CH_4 concentrations were calculated by correcting for average temperature between sampling time as well as dilution that occurred when adding ambient air to samples that were less than 20 mL. This sampling occurred from June 14th until October 10th, 2019. In total, 230 measurements of ebullition CH_4 concentration were collected from the funnels over this period. A smaller sample size was collected from the willow area due to greater water table fluctuations compared to the other locations (Table 2.3). Additionally, less sampling occurred in October as gas samples were only collected until October 10th.

2.2.4 Pore Water Methane Concentrations

A total of eight pore water samplers, four at each depth, were located within each sampling area at depths 15 cm and 40 cm below the peat surface. These samplers were constructed by cutting PVC pipe (2.54 cm inner diameter) into 20 cm lengths. From 5-15 cm, 0.3 cm diameter holes were drilled and then covered by 250 µm Nitex screening to allow water to enter the sampler while preventing clogging from possible peat accumulation. A cap was then placed on each end. One cap then had a hole drilled in it and Tygon tubing was fed into the PVC pipe with a three-way valve on the other end that remained above the surface (Mahmood & Strack, 2011). A 60 mL syringe was used to extract water from these depths after first purging the tubing to ensure that water from the sampler was being collected. Next, a 20 mL sample of water was taken and kept in the syringe. Following this, 20 mL of ambient air was added into the syringe and then shaken for five minutes to transfer any dissolved gases that were present in the water into the ambient air. Once shaking was complete, the 20 mL of air was injected into an Exetainer and then later analyzed on the GC. CH_4 concentrations were corrected for air temperature at the time of collection and pore water concentration was determined according to Kampbell and Vandegrift (1998). These samples were collected to gain a greater understanding of the subsurface CH_4

pools that exist beneath the surface in the various funnel trap locations. Pore water CH_4 concentrations were sampled every week from May-August and then bi-weekly in September and October.

2.2.5 Environmental Variables

Soil temperature at ~15 cm was recorded hourly at each central location using copper-constantan thermocouple wire that was connected to a datalogger (CR1000, Campbell Scientific Canada). Water table level was continuously logged at the same time interval by a levelogger (Solinst Ltd.) that was placed inside a water well near the middle of the fen (sedge location) and corrected for barometric pressure changes using a barologger (Solinst Ltd.). Additionally, centralized water table measurements at each sampling location were recorded whenever ebullition was measured by using a blowpipe inside a water well made from PVC pipe. A tipping bucket was set up within the fen which recorded precipitation hourly. However, this was not set up until June 16th, and precipitation amounts were needed from May 15th up until this date. To deal with this gap in data, precipitation amounts were taken from The Weather Network (https://www.theweathernetwork.com/ca/weather/ontario/puslinch) for the township of Puslinch which is where this fen resides, and future precipitation amounts were compared with tipping bucket data to confirm similar precipitation measurements.

A Russian Corer was used to collect three replicate peat core samples at each of the three central funnel locations. Peat samples were taken until a layer of clay was reached. These peat cores were then sectioned into 5 cm intervals to determine how bulk density and organic matter content changed throughout the peat profile. The corer was unable to successfully sample the top 20 cm of peat due to the dense sedge roots, so this was collected by carefully cutting out a sample using a breadknife. However, since this technique was needed, the 15-20 cm depth section of peat was unable to be collected as it was compressed during core removal. Peat samples were then weighed and dried in a drying oven for 2-3 days at 60 °C to ensure a constant weight had been achieved. Once dried, the samples were then weighed again and bulk density was calculated by dividing the dried weight by the total volume of each sample (Lewis et al., 2012). Approximately 2 g of the dried samples (precise weight was recorded) were then placed in a crucible and burned in a muffle furnace for 3 hours at 550 °C. Once the samples were cooled, they were weighed again to determine loss on ignition. Organic matter content was then calculated by taking the mass lost divided by the initial sample weight.

2.2.6 Peat Core Sample Collection and Experiment Setup

On July 3rd, 2019, three peat cores from three different primary vascular vegetation types (n=9) were taken from Fletcher Creek Ecological Preserve. The samples were extracted using 20 cm inner diameter, 45 cm long PVC pipe. The PVC pipe was placed in an area of the desired vegetation type, and then rubber mallets and a sledgehammer were used to gently lower the pipe until it was flush with the surface. Compression during sampling was minimal (< 5 cm). Afterwards, the PVC pipe was removed from the ground by digging around the pipe, sawing underneath the base and carefully lifting it from the ground without disturbing the contents in the pipe. When a peat core was extracted from the ground, a rubber cap (Fernco) was placed on the bottom of each to stabilize the cores and maintain saturated conditions. Once extraction was completed, the peat cores were immediately transported and placed in a greenhouse located at the University of Waterloo.

Since CH_4 production can be heavily influenced by the anoxic zone in peat, it was important to ensure that a steady water table level would be maintained in each individual peat core. Additionally, since vegetation type varied between the peat cores, the amount of water consumption and evapotranspiration of each peat core differed. Due to these conditions, the experiment was designed (Figure 2.1) to use mariotte regulators to maintain consistent and equal water table levels among all peat cores. A water table level of 1 cm below the surface was chosen to keep potential oxidation of any CH_4, specifically ebullition, to a minimum while avoiding flooding. Additionally, to keep the peat's water chemistry consistent from its natural state, water from a stream that runs through the fen was collected and used in the regulators for the entirety of this experiment.

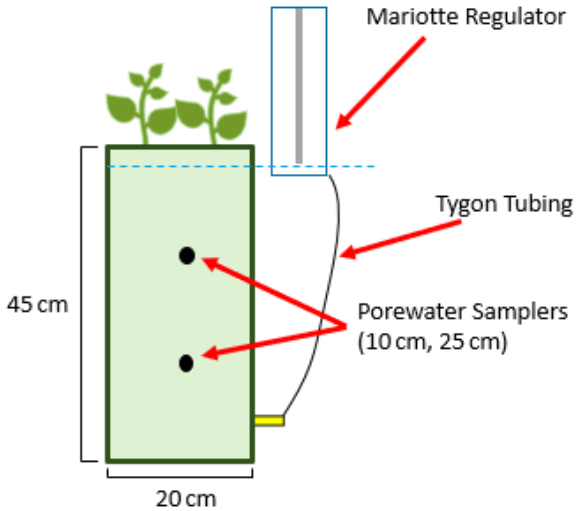

Figure 2.1: Schematic diagram of the greenhouse set up for each individual core.

On August 8th, 2019, the peat cores were temporarily drained for 24 hours when connecting the mariotte regulators as well as installing pore water samplers. Vegetation was given approximately three months to grow and fully establish itself before measurements began on October 1st, 2019. This also provided time for the microbial community to re-stabilize to the saturated conditions. Unfortunately, for the peat core labelled 'W1', the *Salix* that was present in the sample had its roots severed during extraction and it did not survive. This resulted in that specific peat core having a deceased Salix; however, it was maintained throughout the study as it still represented peat properties/root structure associated with the other willow cores.

Over the course of the experiment, temperature in the greenhouse ranged from 17.7 to 42.2 °C, with an overall average temperature of 24.9 °C. Blinds that were attached to the greenhouse windows were used to help regulate temperature within the greenhouse which resulted in photosynthetically active radiation values ranging from 27-1257 W m^{-2}. Additionally, artificial high intensity discharge lights were used to ensure that each peat core received 14 hours of sunlight each day.

2.2.7 Subsurface Methane Pools

Pools of high concentrations of CH_4 are needed in order for free-phase gas to accumulate and ebullition to occur. To examine how this differed between each peat core, pore water samplers were installed at 10 and 25 cm depths. These pore water samplers were constructed using 1.27 cm inner diameter plastic pipe that was cut into 7 cm long sections. Holes were then drilled into the side of the pipe and wrapped with fine mesh (~0.1 cm^2) to prevent clogging. A brass fitting was threaded into each sampler and attached to Tygon tubing with a three-way valve on the end. Pore water samples from each depth were then taken using a 60 mL syringe and later analyzed to determine CH_4 concentrations as described for the field samples. Sampling took place once a week when CH_4 flux measurements occurred (section 2.2.8).

2.2.8 Methane Fluxes and Ebullition Events for Greenhouse Experiment

Methane flux was measured from October 1st until November 29th on a weekly basis. A closed chamber method (Alm et al., 2007) was used with a clear plastic chamber (diameter = 20 cm, height = 40 cm) and a plastic collar (diameter = 19 cm, height = 0.15 cm). A battery powered fan was located at the top of the chamber to create air circulation while a hole that was drilled on the side of the chamber was blocked with a rubber stopper that was fitted with thermocouple wire as well as tubes that were used to measure greenhouse gas concentrations. CH_4 concentration in parts per million within the chamber was

recorded every second using an Ultraportable Greenhouse Gas Analyzer (Los Gatos Research). Meanwhile, temperature was recorded at the beginning and end of each flux. One flux would consist of the chamber sitting on one peat core for five consecutive minutes. Once five minutes passed, the chamber was removed to bring temperature and CH_4 concentration back to ambient. This process was repeated three times for each peat core whenever flux measurements occurred. This resulted in three, five-minute fluxes for each peat sample on each sampling day. In total, 99 fluxes were completed for each peat core type (33 for each individual core).

To determine the CH_4 flux of a peat core, the linear change in CH_4 concentrations over time was calculated and corrected individually based on temperature and chamber headspace. The R^2 value of linear change was also checked and confirmed that it was above 0.75, which was true for all fluxes. To classify ebullition events as occurring, criteria were developed based on the visual interpretation of the flux data. An ebullition event was characterized by a sudden increase in the slope of CH_4 concentration that was greater than 0.1 ppm per second for at least 5 seconds. The magnitude of these ebullition events was then calculated by using a piecewise linear fitting procedure by comparing the slope from before the event and while the event was occurring (Goodrich et al., 2011). The standard flux slope was then subtracted from the ebullition slope to determine the additional CH_4 release attributed to ebullition that occurred within the specific time frame of the event. This was then converted to a mass of CH_4 released (mg CH_4 m^{-2}) by using temperature and chamber volume (Goodrich et al., 2011). Anytime ebullition was present during a flux it was omitted when calculating the overall steady flux (consistent CH_4 release, i.e. diffusion, plant mediated transportation) for that measurement.

2.2.9 Biomass Sampling

All living aboveground biomass was collected from each core at the end of the experiment. Individual plants were clipped as close to the peat surface as possible and separated based on genus. Vegetation was then dried for 72 hours at 60 °C and weighed afterwards to determine aboveground biomass for each peat core. The below ground biomass (roots) of each peat core was also measured. Once aboveground biomass was clipped, peat cores were drained to the 25 cm depth and then frozen. Once frozen, each core was cut 15 and 30 cm from the peat surface using a router and reciprocating saw. This resulted in each core being separated into sections of 0-15 cm, 15-30 cm, and 30-45 cm. Once each peat core had been cut, a quarter of each individual section was taken for root processing. Due to the sheer number of roots found in each sample, only living roots that were 0.25 cm or larger in

diameter were picked from the peat samples using tweezers. Afterwards they were dried at 60 °C for 72 hours and then weighed (Moore et al., 2002).

2.2.10 Bulk Density and Organic Matter

From the peat that was not used for processing below ground biomass, a small piece was cut and measured to determine its volume. Afterwards, bulk density and organic matter content of the subsample was determined as described earlier for the field peat core samples.

2.2.11 Statistical Analysis

A one-way ANOVA was performed on field environmental variables such as soil temperature at 15 cm and pore water CH_4 concentration at 15 and 40 cm to determine if any significant differences were present between each location. In some instances, data was log transformed to improve normality and homogeneity when running statistical analysis. Since repeated measurements were made in the same location over the course of 5 months, linear mixed effects (LME) models from the nlme package (Pinheiro et al., 2018) were initially used in R (R Core Team, 2019) with either having location grouping or month as a fixed factor and funnel as a random factor. Each LME was inspected visually to evaluate normality and homogeneity of residuals. When comparing ebullition fluxes and volume among locations, the LME did not pass for homogeneity. Thus, a Kruskal-Wallis rank sum test from the package plyr (Wickham, 2011) was performed and post hoc analysis was completed using the Dunn Test from the package dunn.test (Dinno, 2017) with p values being adjusted by the 'bonferonni' method. An LME was used to determine ebullition fluxes and volume differences among months by setting month as a fixed factor and funnel as a random factor. Similarly, location ebullition fluxes and volume were compared within each individual month by sub-setting the data and using an LME with location as a fixed factor and funnel as a random factor. When significant differences were found, a Tukey pairwise comparison from the package multcomp (Hothorn et al., 2008) was used to determine where these significant differences existed. A statistical significance level of $\alpha = 0.05$ was used for all statistical tests. The ANOVA command in R was used for all F-values that are reported within this study.

An LME model was also constructed to determine if any significant environmental controls of ebullition fluxes and volume existed across the entire sampling period. Initially a full model was run with location, soil temperature, water table, precipitation and pore water CH_4 concentration at 15 and 40 cm as fixed factors and funnels as a random factor. Two-way interactions between each pair of fixed factors were also included in the model. As pore water CH_4 concentration was not measured adjacent to each

funnel, for the LME the average pore water CH_4 concentrations at each depth in every location for that given sampling day was determined. This averaged value for each location at both depths were then assigned to all funnels within that given area. Water table measurements taken from each sampling location on the day of measurements were assigned to each funnel within each given sampling area. Once the initial model was run, non-significant variables were removed one by one starting with the least significant (i.e., highest p-value). However, if a variable was found to be significant in a two-way interaction with another variable but not on its own, that individual variable was kept in the model. Initially, slight heterogeneity was detected in both models but a varIdent variance structure was applied by location and added to the model to improve overall homogeneity and normality of residuals (Zuur et al., 2009). Additionally, R^2 values provided for LME models were obtained by using the MuMIn package (Barton, 2018).

A Cochran's q test was used to compare ebullition frequencies between different core types from the greenhouse experiment using the R package nonpar (Sweet, 2017). Afterwards, a post hoc Dunn test was used to determine which core types had significant differences. Due to non-normality, a Kruskal-Wallis rank sum test was required to compare ebullition flux between each core type. Again, a post hoc Dunn test was performed if it was determined that there were significant differences. Finally, a one-way ANOVA was used to compare the means of pore water CH_4 concentrations at the depths of 10 and 25 cm for each core type, as well as differences in bulk density and organic matter content.

2.3 Results

2.3.1 Field Results

2.3.1.1 Environmental Conditions

Bulk density increased in each sampling location with depth (Table 2.1). From 0-20 cm, bulk density was relatively similar among locations; however, that changed at depths 20-40 cm and 40-55 cm. The sedge location had the lowest bulk density from 20-40 cm (0.304 g/cm^3) and was significantly lower than the willow location ($F_{2,39}$=9.6, p=0.0003). For 40-55 cm, the stream location had the greatest bulk density (0.583 g/cm^3) and was significantly higher than both the sedge ($F_{2,38}$=10.54, p=0.0003) and the willow ($F_{2,38}$=10.54, p=0.0039) location. The sedge location had the greatest overall organic matter content throughout the peat profile while willow had the least. The sedge sampling area had significantly greater organic matter at 20-40 cm ($F_{2,39}$=12.6, p<0.0001) and 40-55 cm ($F_{2,38}$=29.62, p<0.0001) compared to the other locations.

Table 2.1: Comparison of bulk density and organic matter at different depths and location. Number in brackets represent standard error. Different letters represent a significant difference between locations for each depth, but should not be compared between depths.

Depth (cm)	Sedge		Stream		Willow	
	Bulk Density (g/cm^3)	Organic Matter (%)	Bulk Density (g/cm^3)	Organic Matter (%)	Bulk Density (g/cm^3)	Organic Matter (%)
0-20	0.187 (0.06)^{a}	36.4 (18.0)^{a}	0.187 (0.07)^{a}	42.4 (11.8)^{a}	0.230 (0.06)^{a}	27.0 (6.2)^{a}
20-40	0.304 (0.05)^{a}	67.2 (4.5)^{a}	0.368 (0.10)^{ab}	56.6 (8.2)^{b}	0.429 (0.08)^{b}	54.8 (8.8)^{b}
40-55	0.390 (0.07)^{a}	65.1 (8.7)^{a}	0.583 (0.17)^{b}	37.8 (12.7)^{b}	0.432 (0.07)^{a}	50.5 (4.0)^{c}

Soil temperature at 15 cm depth was not significantly different among locations ($F_{2,71}$=3.1, p=0.0534) (Table 2.2). Average water table over the course of sampling was the highest at the sedge area (1.1 cm, indicating slightly flooded conditions) and significantly higher ($F_{2,65}$=4.8, p=0.0118) than the willow area. Similarly, for pore water CH_4 concentration at 15 cm, the sedge location had the greatest average (2.37 mg/L) and significant difference was found amongst all locations ($F_{2,55}$=33.1, p<0.0001) with the stream area having the lowest concentration. In contrast, for pore water CH_4 concentration at 40 cm, significant differences were found between the stream and willow location ($F_{2,55}$=4.9, p=0.0085) with the average concentration being the greatest in the willow location (3.03 mg/L) and lowest in the stream location (1.79 mg/L).

Table 2.2: Environmental variable averages for each location. Numbers in brackets represent standard error. Varying letters represents a significant difference.

Location	Soil Temperature (°C) 15 cm	Water Table (cm)	Pore Water CH_4 15 cm (mg/L)	Pore Water CH_4 40 cm (mg/L)
Sedge	13.2 (0.45)^{a}	1.1 (0.98)^{a}	2.37 (0.26)^{a}	2.27 (0.15)^{ab}
Stream	13.3 (0.45)^{a}	-3.4 (1.68)^{ab}	0.36 (0.07)^{b}	1.79 (0.19)^{a}
Willow	14.8 (0.56)^{a}	-4.8 (1.48)^{b}	0.97 (0.15)^{c}	3.03 (0.42)^{b}

2.3.1.2 Ebullition Volume and Fluxes

Ebullition amounts were recorded from funnel traps on a weekly basis from March 17th to October 25th while the concentration of CH_4 from these traps were collected from June 14th to October 10th. Over the course of this entire sampling period, the volume of ebullition that occurred was significantly different among all locations (Kruskal-Wallis rank sum test, p<0.0001) (Figure 2.2). The same

was found for the concentration of CH_4 that was released from these locations (Kruskal-Wallis rank sum test, $p<0.0001$). Overall, the sedge location had the greatest average volume of ebullition (93.3 mL m^{-2} d^{-1}) while the willow location had the least (28.8 mL m^{-2} d^{-1}). The same trend was found for the overall average of CH_4 flux from ebullition (Table 2.3). The sedge area released the greatest amount of CH_4 through ebullition at an average rate of 24.2 mg CH_4 m^{-2} d^{-1} over the course of the sampling period while the willow location released only 2.0 mg CH_4 m^{-2} d^{-1}.

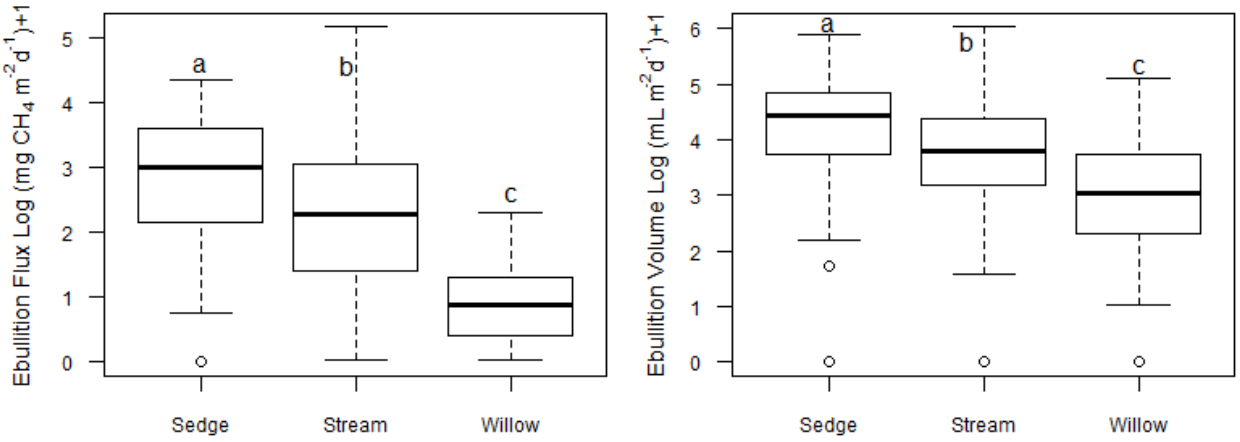

Figure 2.2: Boxplot on the left shows a comparison between ebullition CH_4 flux for each location over the course of the sampling period. Boxplot on the right is a comparison of ebullition volume between locations. Differing letters represent significant difference.

Ebullition volume was not similar among all locations for any month (Figure 2.3). Overall, volume of ebullition was the greatest in August for all three locations while both the sedge and stream area experienced the least in May, but the willow location had the least in October. The sedge area consistently had higher ebullition volume while the willow area had the lowest over the course of sampling. The stream area was intermediate and statistically similar to the sedge area in all months except for June. Regarding monthly values, volumes were significantly different from one another except for July and August ($F_{5,527}=68.3$, $p=0.1235$) as well as July and September ($F_{5,527}=68.3$, $p=0.7922$).

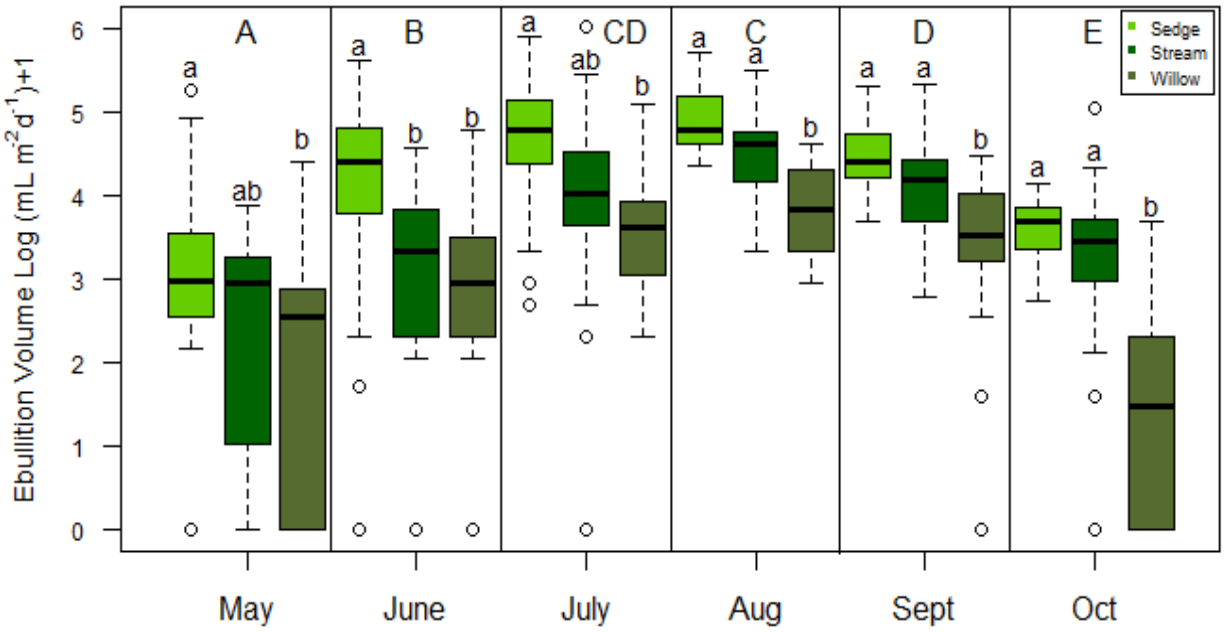

Figure 2.3: Comparison of volume of ebullition based on month and location. Volume was compared against location during each individual month as well overall volume being compared between each month. Capital letters that are different represent significant difference between months while lower case is comparing between location for each month. Note the axis is on a log scale, non-log transformed values can be found in Table 2.3.

The average amount of CH_4 emitted to the atmosphere via ebullition also varied both spatially and temporarily (Figure 2.4). The sedge location consistently had the greatest average emissions each month except for October when the greatest emissions occurred in the stream area (12.9 mg CH_4 m^{-2} d^{-1}). The willow area had significantly less CH_4 emission from ebullition compared to the other locations each month except for in June when no significant difference was found between the willow and stream area ($F_{2,19}$=15.1, p=0.4818). Ebullition CH_4 emissions were overall the greatest in August for both the sedge and stream location but the greatest in July for the willow area. While ebullition was the greatest for the month of August, it appears as if peak ebullition occurred from late July and into early August. Meanwhile, the lowest average emissions occurred in October for the sedge and willow area while the stream location had the lowest in June. Comparing CH_4 emissions from ebullition for each month, several months were found to be significantly different from one another ($F_{4,198}$=36.3, p<0.0001). There appears to be a rising trend from June-August while emissions begin to decline afterwards.

Table 2.3: Monthly average CH_4 fluxes from ebullition as well as volume for each location. Number in brackets represent standard error. Standard error is quite high for volume of ebullition as there was a wide range of volumes for each month. Varying letters represents significant differences between location for each month and should not be compared between months. Total possible ebullition volume recordings for each month from May-October were 27, 54, 45, 36, 36 and 27 respectively. Maximum recordings were not achieved due to changing of water table levels which would cause water and gas to be released from the funnels.

Location	Ebullition	Month						Overall
		May	June	July	August	September	October	
Sedge	Ebullition Flux (mg CH_4 m^{-2} d^{-1})	*N/A*	15.1 (4.27)[a]	31.6 (4.69)[a]	40.2 (4.87)[a]	19.9 (2.47)[a]	5.1 (1.67)[a]	24.2 (2.19)[a]
	Sample Size (n)	*N/A*	17	21	16	20	9	83
	Ebullition volume (mL m^{-2} d^{-1})	32.5 (41.45)[a]	92.3 (66.04)[a]	126.3 (74.20)[a]	141.5 (57.20)[a]	95.3 (38.91)[a]	37.8 (13.09)[a]	93.3 (4.55)[a]
	Sample Size (n)	26	51	41	36	35	27	216
Stream	Ebullition Flux (mg CH_4 m^{-2} d^{-1})	*N/A*	2.0 (0.40)[b]	23.8 (7.97)[a]	24.2 (5.15)[a]	14.1 (2.85)[a]	12.9 (6.70)[a]	17.2 (2.72)[b]
	Sample Size (n)	*N/A*	12	22	21	20	10	85
	Ebullition volume (mL m^{-2} d^{-1})	16.5 (13.67)[ab]	31.9 (25.24)[b]	78.3 (75.87)[ab]	98.9 (49.35)[a]	72.1 (48.47)[a]	34.2 (30.18)[a]	58.6 (3.95)[b]
	Sample Size (n)	19	41	36	34	35	27	192
Willow	Ebullition Flux (mg CH_4 m^{-2} d^{-1})	*N/A*	1.0 (0.21)[b]	3.1 (0.85)[b]	2.9 (0.59)[b]	1.4 (0.36)[b]	1.0 (0.19)[b]	2.0 (0.26)[c]
	Sample Size (n)	*N/A*	16	12	15	14	5	62
	Ebullition volume (mL m^{-2} d^{-1})	12.3 (16.41)[b]	25.6 (23.82)[b]	44.4 (35.08)[b]	51.6 (25.95)[b]	37.9 (22.16)[b]	8.0 (10.98)[b]	28.8 (2.18)[c]
	Sample Size (n)	27	48	23	22	20	21	161

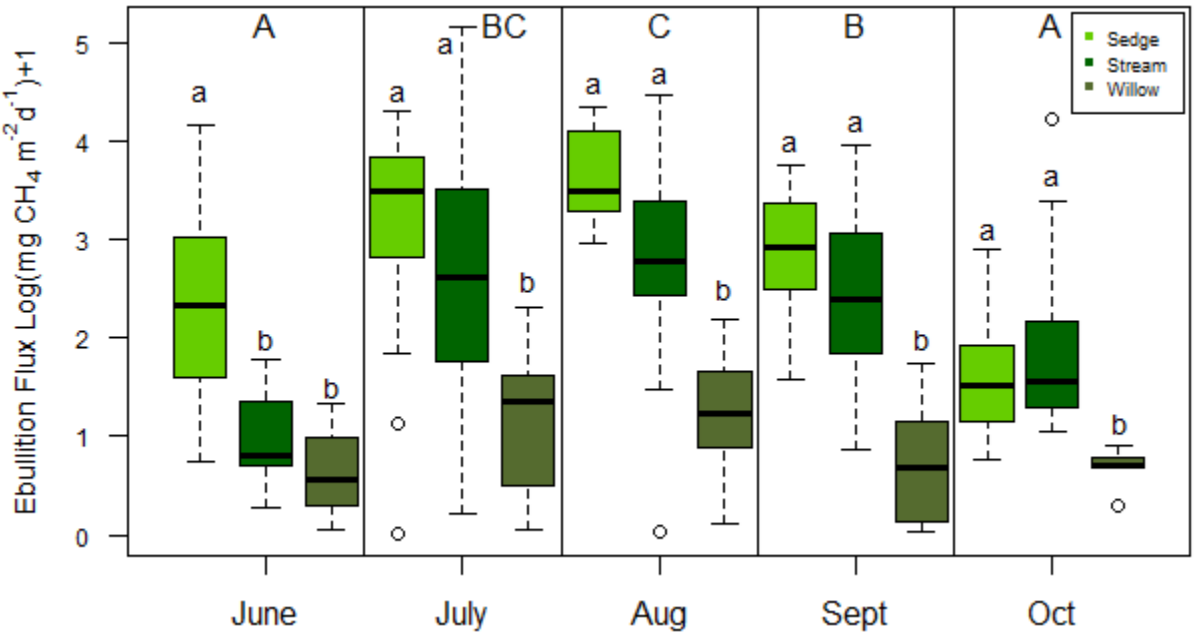

Figure 2.4: Comparison of CH_4 emissions from ebullition based on month and location. Emissions were compared against location during each individual month and a differing lower-case letter represents a significant difference. Differing capital letters represent a significant difference between months for all ebullition fluxes. Note the axis is on a log scale, non-log transformed values can be found in Table 2.3.

2.3.1.3 Environmental Controls on Ebullition

A time series scatterplot of average ebullition volume per day was graphed alongside atmospheric pressure and water table levels to determine if consistent changes in either of these variables influenced the amount of ebullition that occurred over the course of the sampling period. While ebullition sampling only took place typically on a weekly scale and not at a higher temporal resolution, there were still a few instances where it appears that consistent changes in atmospheric pressure and water table over time either increased or decreased ebullition release.

For atmospheric pressure, there was a period from mid to late September that had a rather large decrease in atmospheric pressure that appears to correspond with a large increase in ebullition release (Figure 2.5). From day of year (DOY) 256-268, atmospheric pressure dropped from 98.9 to 97.4 kPa. This resulted in an average ebullition volume per day increase from 43.1 to 105.8 mL m^{-2} d^{-1}. Additionally, the greatest average volume of ebullition release during the sampling period also occurred after a drop in atmospheric pressure. From DOY 212-221, atmospheric pressure dropped from 98.7 to 97.6 kPa and ebullition increased from 109 to 125.5 mL m^{-2} d^{-1}. On the contrary, there was one instance where a consistent increase of atmospheric pressure corresponded with a large increase in ebullition

volume. This occurred from DOY 199-205, atmospheric pressure rose from 97.6 to 98.3 kPa and ebullition volume saw an increase from 61.9 to 111.3 mL m^{-2} d^{-1}.

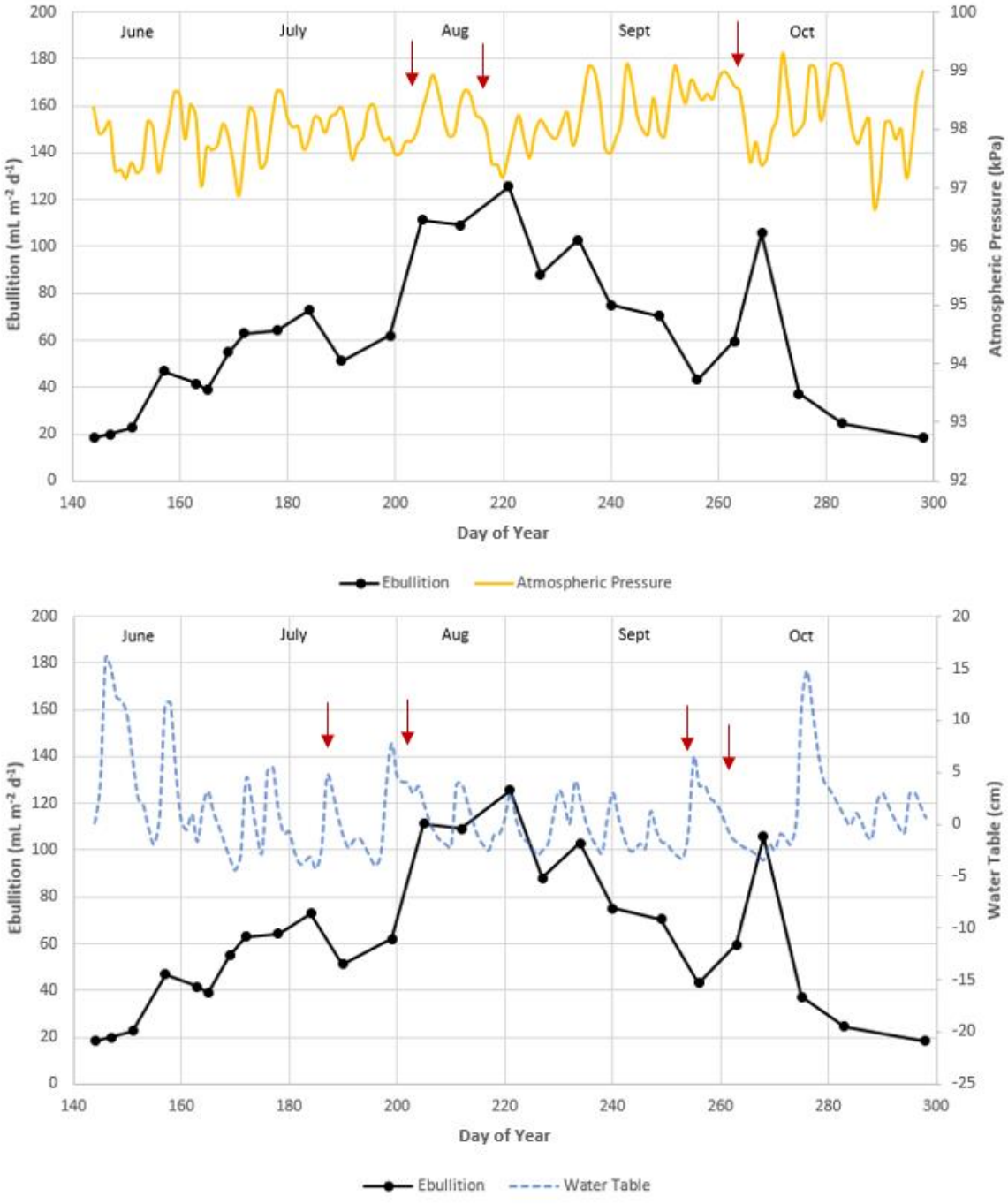

Figure 2.5: The top graph represents a time series scatter plot graph over the course of the sampling period for ebullition volume averages (all sampling locations combined) and atmospheric pressure. The bottom is a scatter plot graph of water table and average ebullition volume over the course of the sampling period. Arrows highlights the timeframes that were discussed in the text.

With water table, there were a few instances where a consistent decrease in water table led to an overall increase in ebullition volume (Figure 2.5). For example, from DOY 199-205, water table levels dropped from 7.8 to 3.7 cm which corresponded with an increase from 62 to 111.3 mL m^{-2} d^{-1} for ebullition volume. The same time frame was previously mentioned as a period of time when an increase in atmospheric pressure corresponded with this increase in ebullition volume, which is not typically expected. It is possible that this sudden rise in ebullition was caused by the declining water table rather than the increase of atmospheric pressure. Another large increase of ebullition volume occurred from DOY 256-268. Water table levels dropped from 3.7 to -3.4 cm, while average ebullition volume increased from 43.1 to 105.8 mL m^{-2} d^{-1} over this time period. While water table levels did drop during this time, so did atmospheric pressure. It is possible that both factors contributed to the large increase of ebullition release during this time. Opposite to water table decrease, there appears to be two clear time periods where consistent water table increase potentially limited ebullition release. From DOY 184-190, the water table was lowest at -4.3 and greatest at 4.7 cm and average ebullition volume decreased from 72.9 to 51.0 mL m^{-2} d^{-1}. Likewise, over the course of DOY 249-253, water table rose from -3.2 to 6.5 cm and average ebullition volume dropped from 70.3 to 43.1 mL m^{-2} d^{-1}.

Using a linear mixed effects model, it was determined that several variables and interaction of variables explained a significant amount of the variability in ebullition (Table 2.4). Location, soil temperature, precipitation, pore water concentration at 15 cm and pore water concentration at 40 cm were all found to be significantly related to ebullition CH_4 fluxes. Additionally, interactions between water table and precipitation, as well as location and soil temperature were also deemed significant.

Table 2.4: Statistical results of LME used to determine relationships between environmental variables. The model originally started with location, soil temperature, water table, precipitation, pore water concentration at 15 and 40 cm as well as two-way interactions between each. Nonsignificant relationships were removed, however if a variable was considered significant in an interaction it was kept in the model.

	Variable	F	*p*	R^2m	R^2c
Ebullition Flux	Location	$F_{2,24} = 28.4$	**<0.0001**	65.4	82.1
	Soil Temperature	$F_{1,131} = 144.3$	**<0.0001**		
	Precipitation	$F_{1,131} = 39.8$	**<0.0001**		
	Pore Water 15 cm	$F_{1,131} = 7.2$	**0.0082**		
	Pore Water 40 cm	$F_{1,131} = 6.7$	**0.0106**		
	Water Table	$F_{1,131} = 0.4$	0.5301		
	Water Table x Precipitation	$F_{1,131} = 5.9$	**0.0161**		
	Location x Soil Temperature	$F_{2,131} = 9.9$	**0.0001**		
Ebullition Volume	Location	$F_{2,24} = 15.0$	**0.0001**	42.2	56.8
	Soil Temperature	$F_{1,421} = 287.8$	**<0.0001**		
	Precipitation	$F_{1,421} = 6.7$	**0.0098**		
	Pore Water 40 cm	$F_{1,421} = 2.0$	0.1530		
	Location x Soil Temperature	$F_{1,421} = 5.1$	**0.0067**		
	Location x Pore Water 40 cm	$F_{1,421} = 7.4$	**0.0007**		

Soil temperature, when viewed based on location, clearly shows a moderate positive correlation to ebullition flux for all three locations (Figure 2.6). Likewise, pore water CH_4 concentration at 15 cm also had a positive correlation with ebullition fluxes, although it is a weaker relationship. A very similar trend was present for pore water CH_4 concentration at 40 cm. Increasing precipitation amounts were also linked to increasing water table levels that, at times, resulted in the reduction of ebullition flux, which explains the significant relationship between the interaction of water table and precipitation.

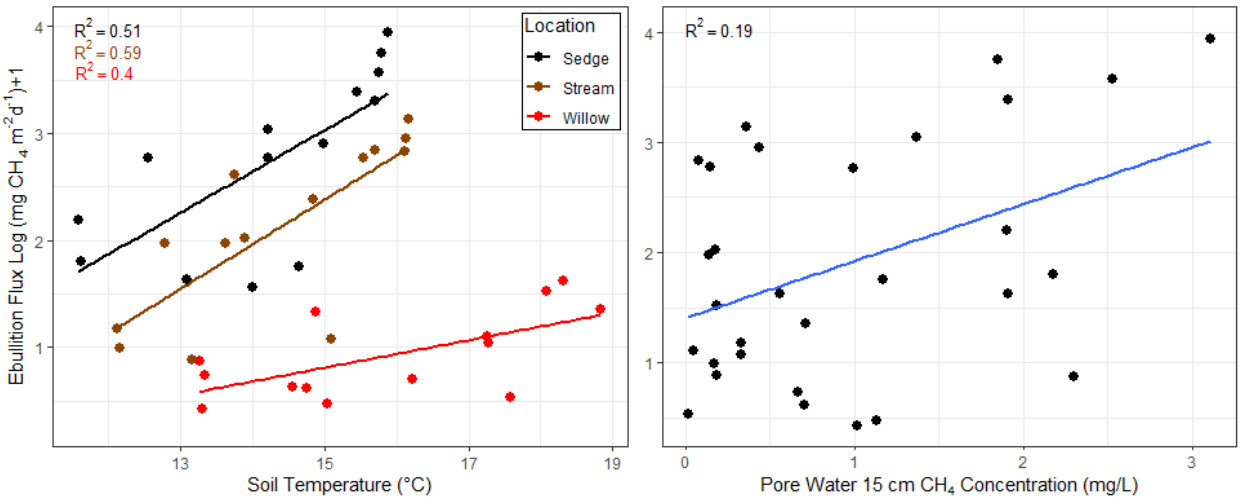

Figure 2.6: Scatter plot on the left shows the relationship between soil temperature at 15 cm and CH_4 fluxes from ebullition. Scatter plot on the right displays the slight positive correlation between pore water CH_4 concentrations at 15 cm and ebullition CH_4 fluxes.

For ebullition volume, location, soil temperature and precipitation as well as the interactions between location and soil temperature and location and pore water CH_4 concentration at 40 cm were all found to be significant factors. Similar to the flux of ebullition, the volume of ebullition clearly has a moderate positive correlation to soil temperature at all locations. Even though precipitation was considered a significant factor, there appears to be no direct linear correlation with ebullition volume itself (Figure 2.7).

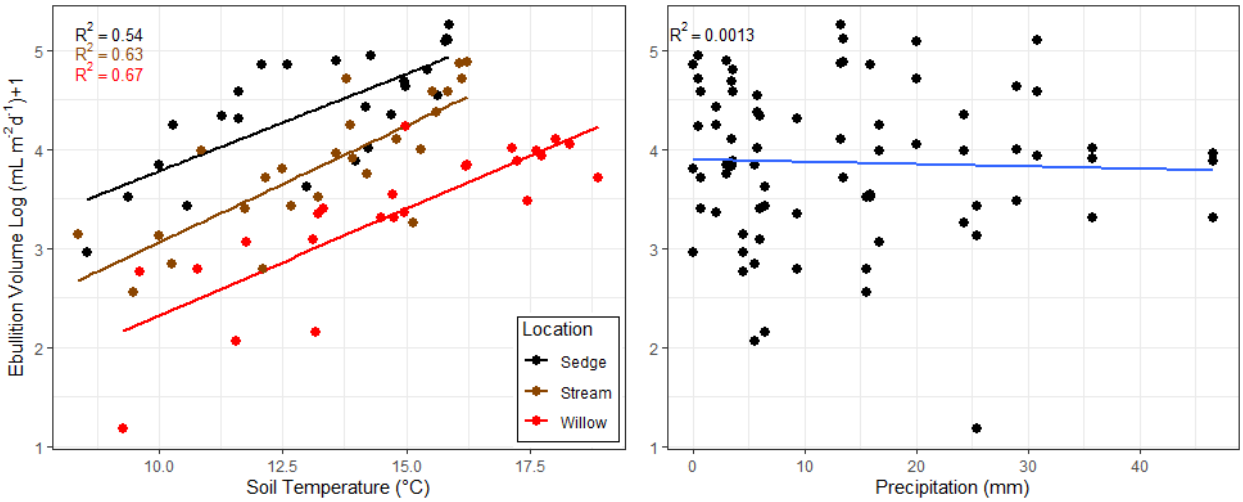

Figure 2.7: Left scatterplot shows the relationship between soil temperature at each different location and ebullition volume. Scatterplot on the right shows the relationship of precipitation and ebullition volume.

For both ebullition volume and fluxes, a large amount of variability is explained by the random factor which can be seen from the differences in R^2m and R^2c. This highlights the innate spatial variability in ebullition, as large variation was found between funnels, with some consistently having higher releases than others.

2.3.2 Greenhouse Experiment Results

2.3.2.1 Vegetation Cover and Biomass

Carex spp. was the most dominant species in the sedge, as well as willow cores (Table 2.5). However, there was a much higher percentage cover of *Carex* in the sedge cores (40-45%) than the willow cores (10-20%). Additionally, the willow cores also had *Salix candida;* however, one was deceased in the 'W1' core due to the roots being severed while extracting the cores. For the bare cores, no vascular plants were ever present during the experiment. However, over time a very fine layer of moss (<0.2 cm in thickness) developed on the cores. The core 'B1' had the greatest amount of moss coverage at 95% while 'B3' had the least with only 2% coverage.

Table 2.5: Vegetation survey for each individual core used in the greenhouse experiment.

Core	Vegetation (%)					Bare (%)	Litter (%)
	***Carex* spp.**	***Salix candida***	***Juncus* spp.**	***Galium trifidum***	**Moss**		
B1					95	2	2
B2					7	80	20
B3					2	98	2
W1	20	Deceased (1)					90
W2	10	2				7	93
W3	15	6	5	Present		12	45
S1	40			Present		17	60
S2	45					15	60
S3	45					5	80

For the vegetated cores, aboveground biomass was the greatest in 'S3' (333.20 g m^{-2}) and the least in 'W1' (57.38 g m^{-2}). Overall, it is clearly apparent that the sedge cores had much greater vascular plant biomass than the willow cores (Table 2.6). The average amount of aboveground biomass for the sedge cores was 259.22 g m^{-2} while the willow cores only averaged 74.09 g m^{-2}. This shows that aboveground vascular plant coverage was approximately 3.5 times greater in the sedge cores than the willow cores.

Table 2.6: Measurements of aboveground biomass for each core.

Core	Vegetation	Aboveground Biomass (g m^{-2})	Total (g m^{-2})
W1	*Carex* spp.	57.38	57.38
W2	*Salix candida* Stems	51.89	90.00
	Salix candida Leaves	2.86	
	Carex spp.	35.25	
W3	*Salix candida* Stems	40.59	74.88
	Salix candida Leaves	5.89	
	Carex spp.	19.18	
	Juncus spp.	8.91	
	Galium trifidum	0.32	
S1	*Carex* spp.	210.49	210.81
	Galium trifidum	0.32	
S2	*Carex* spp.	23.65	233.65
S3	*Carex* spp.	333.20	333.20

Belowground biomass (Table 2.7) for the bare cores was significantly less at 0-15 cm compared to willow and sedge cores ($F_{2,6}$=19.8, p=0.0023). There was also significantly less belowground biomass in bare cores than the sedge cores at 15-30 cm ($F_{2,6}$=11.1, p=0.0079). Regarding overall belowground biomass, the bare cores had the least with only 187.14 g m^{-2} while the sedge cores had the greatest belowground biomass of 1042.27 g m^{-2}. Meanwhile the willow cores fell in the middle of the two with 695.88 g m^{-2} of belowground biomass.

Table 2.7: Amount of belowground biomass of vascular plants that were found in all cores. Belowground biomass significant testing was done between different core types at the same depths. Total belowground biomass is the sum of all the depths combined. Values in bracket represent standard error.

Core Type	Depth (cm)	Belowground Biomass (g m^{-2})	Total Belowground Biomass (g m^{-2})
Bare	0-15	40.11 (4.77)^{a}	187.14 (5.07)
	15-30	10.29 (1.77)^{a}	
	30-45	11.98 (1.38)^{a}	
Willow	0-15	174.23 (39.74)^{b}	695.88 (27.03)
	15-30	34.38 (6.41)^{ab}	
	30-45	23.35 (8.72)^{a}	
Sedge	0-15	256.14 (21.40)^{b}	1042.27 (36.11)
	15-30	60.59 (12.37)^{b}	
	30-45	30.70 (6.26)^{a}	

2.3.2.2 Peat Properties

When comparing bulk density between different core types and depths, the willow cores had a significantly lower bulk density from 15-30 cm than both the bare and sedge cores ($F_{2,6}$=52.7, p=0.0002). Also, from 30-45 cm, the willow cores were significantly less dense than the bare cores ($F_{2,6}$=7.1 p=0.0269). Generally, the willow cores had the lowest bulk density throughout the peat profile while the bare cores had the greatest. Organic matter content was similar between the cores except at 15-30 cm where willow cores had significantly greater amounts (Table 2.8; $F_{2,6}$=20.9, p=0.002).

Table 2.8: Average peat profile characteristics for each core type. Bulk density and organic matter were all determined at the depths 0-15, 15-30, 30-45 cm. Significance testing was done between the different core types for the same depth. Different letters indicate a significant difference.

Core Type	Depth (cm)	Bulk Density (g/cm^3)	Organic Matter (%)
Bare	0-15	0.250 (0.015)[a]	48.2 (1.6)[a]
	15-30	0.268 (0.007)[a]	26.6 (1.1)[a]
	30-45	0.239 (0.005)[a]	54.8 (5.9)[a]
Willow	0-15	0.169 (0.028)[a]	53.5 (10.1)[a]
	15-30	0.124 (0.016)[b]	78.0 (0.3)[b]
	30-45	0.136 (0.024)[b]	68.7 (5.0)[a]
Sedge	0-15	0.235 (0.024)[a]	43.6 (9.6)[a]
	15-30	0.229 (0.005)[a]	38.6 (10.1)[a]
	30-45	0.218 (0.026)[ab]	53.2 (4.6)[a]

2.3.2.3 Pore Water Methane Pools

Pore water CH_4 concentration at 10 cm was significantly different among all core types as seen in Figure 2.8 ($F_{2,6}$=74.8, p<0.0001). The bare cores had the highest average concentration of 25.85 mg/L while the willow and sedge cores had an average of 13.77 and 2.18 mg/L, respectively. A slightly different trend was found for pore water CH_4 concentration at 25 cm. A significant difference was found between the sedge and both the bare and willow cores ($F_{2,6}$=57.2, p=0.0001). At this depth, the willow cores had the highest average concentration of 17.03 mg/L while the bare cores had a slightly lower average of 15.96 mg/L. With an average pore water CH_4 concentration of 3.88 mg/L, the sedge cores had a much lower average compared to the other core types.

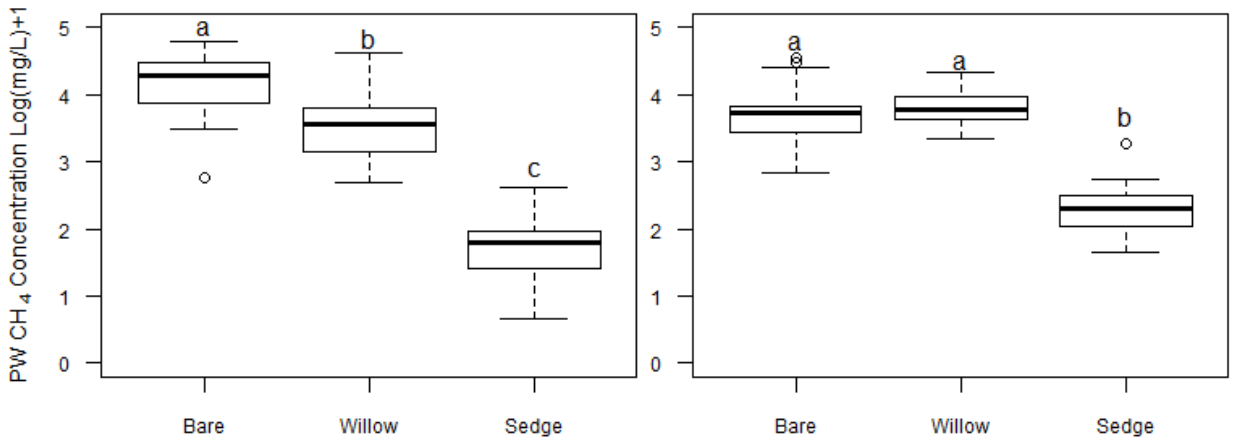

Figure 2.8: Box plots comparing pore water CH_4 concentration at 10 cm (left) and 25 cm (right). Opposing letters represents a significant difference, but should not be compared between plots.

Belowground biomass had a negative relationship with pore water CH_4 concentration at both depths (Figure 2.9). A moderate linear relationship (R^2=0.48) was found for pore water CH_4 concentration at 25 cm while a strong linear relationship (R^2=0.84) was found for pore water CH_4 concentration at 10 cm.

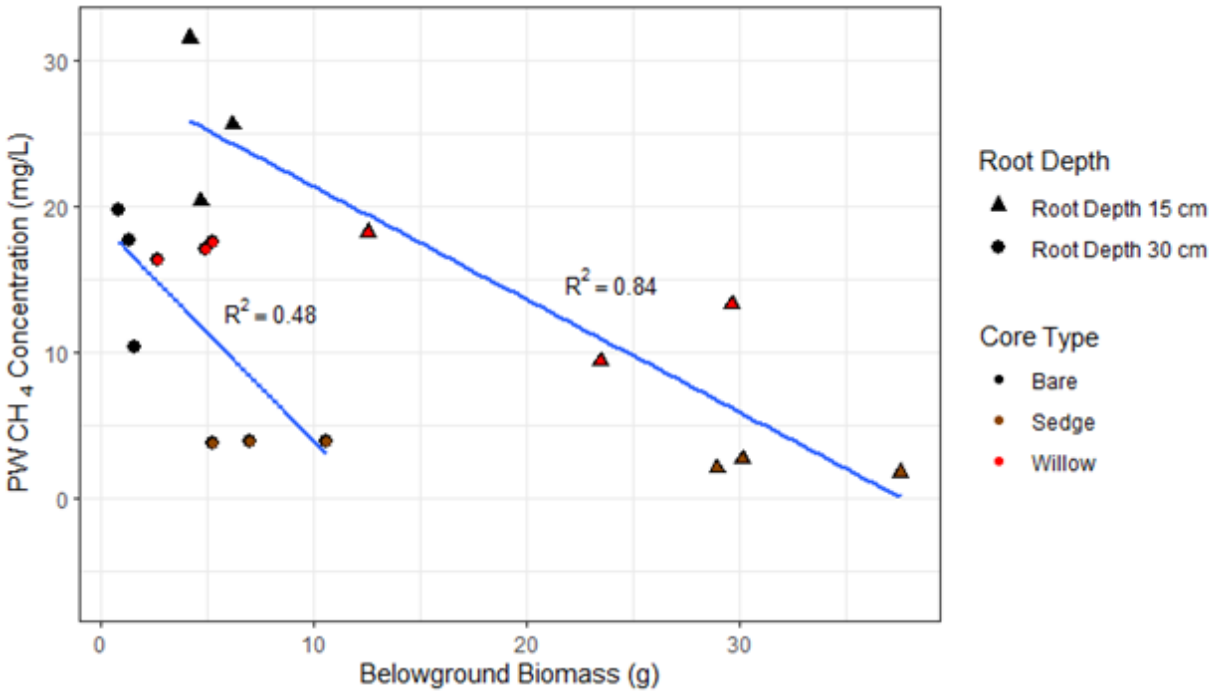

Figure 2.9: Scatterplot graph showing the correlation between belowground biomass and pore water CH_4 concentration at the two depths of the pore water samples. Root depth at 15 cm: y=-0.76x + 28.77. Root depth at 30 cm: y=-1.50x + 18.91.

2.3.2.4 Ebullition Comparison

Over the course of the entire experiment, a total of 99, 5-minute fluxes were performed on each core type (33 on each individual core). While one of the willow cores contained a deceased willow, it was still grouped together with the other willow cores as the rest of the vegetation coverage and amount was similar. If ebullition occurred during one of the 5-minute flux periods, it was identified and separated from the typical diffusive and plant mediated flux (i.e., steady flux) of CH_4. The number of fluxes that contained ebullition varied among core types. The willow cores experienced the most frequent ebullition as 17 out of the 99 fluxes contained some sort of ebullition. The bare cores were similar, as 16 out of the 99 fluxes had ebullition. Meanwhile, ebullition only occurred 3 times total in the sedge cores over the course of 99 fluxes. Using a Cochran's Q Test it was determined that ebullition occurred at a significantly higher frequency in the bare and willow cores compared to the sedge (p=0.0015).

On average, CH_4 emitted from ebullition events that occurred in the bare cores was the highest at 44.4 mg CH_4 m^{-2} hr^{-1} with the willow cores not far behind at 33.7 mg CH_4 m^{-2} hr^{-1}. The sedge cores had the lowest average ebullition flux of 11.9 mg CH_4 m^{-2} hr^{-1}. Additionally, the bare cores also had the single highest ebullition event which was 172.1 mg CH_4 m^{-2} hr^{-1}. The greatest captured ebullition event for the willow cores was 91.8 mg CH_4 m^{-2} hr^{-1} and only 23.7 mg CH_4 m^{-2} hr^{-1} for the sedge cores. When comparing ebullition amounts between core types (Figure 2.10), significantly lower emissions were found at sedge compared to both the bare and willow cores (Kruskal-Wallis Rank Sum Test, p=0.0027). It is important to note that these values are based on the calculated ebullition values and do not include the flux runs where ebullition was zero (not present).

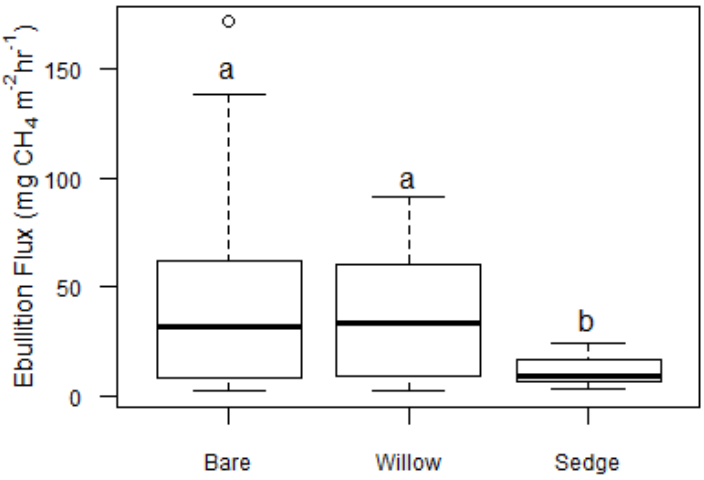

Figure 2.10: Comparison of all ebullition CH_4 fluxes between different core types that were observed over the course of the entire experiment. This figure only includes ebullition that was observed and calculated. It does not include the fluxes where ebullition would have been zero. Differing letters represents a significant difference.

While the sedge cores lacked in ebullition, they released the greatest amount of CH_4 through steady flux throughout the entire duration of the study (Table 2.9). The amount of CH_4 released through these pathways was 67.0, 151.4 and 152.1 mg CH_4 m^{-2} for the bare, willow and sedge cores, respectively. Meanwhile, for ebullition, the bare cores released the greatest amount of CH_4 at a rate of 59.2 mg CH_4 m^{-2} while the willow and sedge cores released 53.3 and 3.0 mg CH_4 m^{-2}, respectively. In total, over the course of 595 minutes of flux measurements, a total of 126.2, 204.7 and 155.1 mg CH_4 m^{-2} were released from the bare, willow and sedge core types, respectively. This resulted in ebullition representing 46.9% of CH_4 released from the bare cores, 26.1% for the willow cores and only 1.9% for the sedge cores.

Table 2.9: The sum of the amount of CH_4 that was released from each core type over the course of 495 minutes of fluxing. Percentage of CH_4 released by ebullition as well as steady flux are also shown. Numbers in brackets represent the standard errors of the mean for each flux run. Ebullition standard error is calculated based on ebullition that was present, it is excluding the runs where it was zero.

Core Type	Total Steady Flux (mg CH_4 m^{-2})	Total Ebullition (mg CH_4 m^{-2})	Total CH_4 emitted (mg CH_4 m^{-2})	Percentage Ebullition (%)
Bare	67.0 (0.06)	59.2 (1.03)	126.2	46.9
Willow	151.4 (0.06)	53.3 (0.63)	204.7	26.1
Sedge	152.1 (0.06)	3.0 (0.51)	155.1	1.9

2.4 Discussion

Ebullition within peatlands has been found to be highly heterogenous and rates of release can vary by orders of magnitude spatiotemporally making it a difficult process to measure (Comas and Wright, 2012). Often, this type of CH_4 release has been ignored when calculating annual CH_4 emissions despite up to 60% of available CH_4 amassing in the form of these bubbles in the peat (Tokida et al., 2005b). Additionally, it has been proven in certain wetlands that ebullition can act as a major contributor to annual CH_4 emissions (20%) and be on par with the amount of diffusion that is occurring (Jeffrey et al., 2019). Despite the difficulties, our models suggest that a large proportion of the variation exhibited by ebullition can be explained by a few frequently measured variables such a soil temperature and pore water CH_4 concentrations. Additionally, precipitation was also able to explain variation as it tends to temporarily reduce ebullition from occurring by increasing hydrostatic pressure.

2.4.1 Peat Properties and Environmental Controls of Ebullition

In this study, both CH_4 emissions from ebullition as well as the amount of ebullition that occurred varied in space and time. Over the course of the entire sampling period, the sedge location had the greatest average of ebullition flux (24.2 mg CH_4 m^{-2} d^{-1}) and volume (93.3 mL m^{-2} d^{-1}). Meanwhile, the willow location had the least in both (2.0 mg CH_4 m^{-2} d^{-1}, 28.8 mL m^{-2} d^{-1}). These results strengthen the fact that that spatial variability is an important factor when measuring ebullition in peatlands as ebullition is not homogeneous (Stanley et al., 2019). Spatial variability was even observed amongst funnels that were within the same grouping (no more than a few meters a part) which was demonstrated by the LME models and the differences between R^2m and R^2c. These discrepancies can possibly be explained by local peat properties and environmental variables such as water table levels or pore water CH_4 concentration. Overall, bulk density was the greatest in the willow sampling location and the least in the sedge location. In past studies, relationships have been found demonstrating that when bulk density increases, the porosity of peat or soil tends to decrease (Kakaire et al., 2015). When porosity decreases, there is less space for bubbles to form, especially larger ones which contain higher volume and CH_4 concentration. Ramirez et al. (2015) found through modeling that peat properties can act as a 'signal shredder', impacting the timing of release and size of ebullition events highlighting the importance that peat structure has on ebullition as a whole. Furthermore, only a small difference (1-4%) in peat porosity is needed to double the amount of gas storage capabilities (Strack and Mierau, 2010). Therefore, the higher bulk density of peat at the stream and willow locations in the field study may have

contributed to lower ebullition amounts observed at these locations by more effectively trapping bubbles and preventing their release.

On top of peat properties, it is likely that differing environmental variables such as water table and pore water CH_4 concentrations further contributed to the discrepancies that were found between each location for both ebullition flux and volume. Overall, the sedge location had the greatest average water table level (1.1 cm) with slightly drier conditions at the stream (-3.4 cm) and willow locations (-4.8 cm). The average amounts of ebullition flux and volume over the course of the sampling period follow the same trend as water table levels. Water table levels have the ability to influence ebullition flux and volume by controlling the size of the oxic and anoxic zones in the peat. With a greater oxic zone, CH_4, including that in free-phase gas, will have a higher chance of being consumed by methanotrophs (Green and Baird, 2012), thus reducing the amount that reaches the surface. The sedge location typically had water table levels that were close to the surface for the duration of the sampling period while that was not true for the sedge and willow locations which more often than not, had water table levels below the surface. This likely led to a decrease in ebullition reaching the surface due to the consumption of CH_4 from methanotrophs. Additionally, a larger anoxic zone found within the sedge area likely meant that a greater number of methanogens were present for the production of CH_4 and thus ebullition. The other variable that likely contributed to the heterogeneity of ebullition spatially was a difference in pore water CH_4 concentrations at 15 cm (Strack et al., 2005). The sedge location (2.37 mg/L) had a significantly higher pore water CH_4 concentration at 15 cm than both the stream (0.36 mg/L) and willow (0.97 mg/L). High concentrations of CH_4 are needed for free phase gas to form (Joyce and Jewell, 2003) and while ebullition is more likely to form deeper in peat, substantial amounts of free phase gas can also be present near the surface (Strack and Mierau, 2010) to assist with the formation of bubbles. Having significantly higher CH_4 concentrations near the surface likely led to the production of more ebullition with higher concentrations of CH_4 near the surface in the sedge location compared to the stream and willow location. Similar trends were also found in the greenhouse experiment. Pore water CH_4 concentrations were significantly lower at both depths for the sedge cores in comparison to the bare and willow which likely resulted in ebullition occurring at a significantly lower frequency, and concentration. Although it appears contradictory that the field sedge location had the greatest pore water CH_4 concentration while the greenhouse sedge cores had the lowest, it is important to note that the overall coverage and size of sedges in the greenhouse experiment were much greater in the sedge cores than the willow cores which likely contributed to lower concentrations in comparison. Such discrepancies of vegetation coverage were not present in the field amongst each sampling location.

An additional variable that might have reduced the amount of ebullition occurring in the willow area that was not measured is the presence of dense woody layers throughout the peat. The funnels in this location were buried near large clumps of *Salix* which likely have rather complex and larger root systems than *Carex*. Dense woody layers present in peat have been shown to confine and restrict ebullition release (Glaser et al., 2004). In addition to higher bulk density, it is possible that the willow area has large root systems and more woody material in the peat which further restricts the movement or formation of bubbles in the first place. Furthermore, the willow location had much lower organic matter content from 0-40 cm compared to the other two locations. This reduction in organic material can lead to a decline of available substrates that are required for CH_4 production. On the contrary, opposite results were found during the greenhouse experiment. Overall, organic matter was the greatest in the willow cores, with it being significantly higher from 15-30 cm compared to the other core types. This is likely a contributing factor as to why the willow cores emitted the most CH_4 overall. In the field, differences in water chemistry among locations is another potential explanation for differing ebullition amounts. CH_4 availability and emissions have been shown to change due to variations in water chemistry (Medvedeff et al., 2014; Gauci et al., 2005; Ye et al., 2012). While water chemistry was not examined, it is clear the hydrologic flow throughout the fen varies as water table levels were not consistent between locations. This difference in flow can lead to a difference in water chemistry and potentially the availability of terminal electron acceptors that may either promote or restrict CH_4 production. Additionally, hyporheic interactions based on the proximity of the stream's and willow's grouping to the tributary stream could have influenced the amount of ongoing ebullition. There is the possibility that water carried by the stream could interact and mix with the ground water present in the peat. Water that is brought in from the stream is likely to be rich in oxygen, which can reduce CH_4 production and enhance oxidation. Furthermore, this mixing of water could move CH_4 out laterally from the peat and into the stream, resulting in a loss of subsurface CH_4.

Rates of ebullition increased collectively with soil temperatures (Figure 2.6 & 2.7), as shown earlier (Kellner et al., 2006; Strack and Waddington, 2008; Goodrich et al., 2011; Männistö et al., 2019). Out of all variables, soil temperature had the highest correlation with ebullition, and ebullition rates appeared to follow the seasonal trends of temperature. This is likely due to the methanogens increasing in activity linearly with temperature until the optimum temperature (25 °C) is reached (Dunfield et al., 1993). Additionally, when temperature increases, CH_4 has a higher likelihood to change from an aqueous to gaseous state leading to bubble formation and expansion due to its reduced solubility (Strack et al.,

2005; Goodrich et al., 2011). Due to this reasoning, it is not a surprise that in this fen ebullition peaked during times when soil temperature was at its highest.

Lower barometric and hydrostatic pressure can also act as important factors for the timing of ebullition as this not only causes gas expansion but also gas formation as it moves out of solution (Fechner-Levy and Hemond, 1996). As more bubbles begin to form, a critical threshold can be crossed that forces bubbles to be released from below the surface. While ebullition was not measured at a very fine temporal resolution for this study, there still appeared to be instances where consistent drops in barometric pressure resulted in an increase in overall ebullition. The greatest amount of ebullition per day over the course of sampling occurred right after there was a relatively large drop in atmospheric pressure in relation to the rest of the sampling period. Additionally, ebullition volume was slowly declining from mid-August to mid-September until another large drop in barometric pressure likely contributed to a sudden spike in ebullition. These results are consistent with several other studies that found sudden drops in barometric pressure led to an increase in ebullition (Glaser et al., 2004; Tokida et al., 2005a; Kellner et al., 2006; Comas et al., 2007; Tokida et al., 2007; Yu et al., 2014). On the contrary, a study completed by Comas and Wright (2012) found that increases in barometric pressure resulted in an increase in ebullition from a subtropical peatland. They attributed this occurrence to high porosity which will increase the movement of bubbles as they become smaller in size due to the pressure increase (Comas and Wright, 2012). While there was an occurrence on DOY 205 when a steady increase in atmospheric pressure resulted in an increase of ebullition volume, it is possible that a decrease in water table (and hence hydrostatic pressure) over the same time period was the dominant cause. Decreases in water table have been shown to increase ebullition in other peatland studies (Strack and Waddington, 2008; Männistö et al., 2019). Additionally, there were also a few instances where increases in water table appeared to reduce overall ebullition volume. This is caused from an increase in hydrostatic pressure which will restrict the movement of bubbles in the peat. To more accurately understand the influence of barometric pressure on ebullition within this fen, measurements would have to be made on a much higher temporal resolution. Measurements taken on a one-week scale makes it difficult to truly investigate the effects that atmospheric pressure may have had on ebullition when several variables could have changed over the same time frame.

2.4.2 Vascular Vegetation Controls on Ebullition

During the greenhouse experiment, the sedge cores had ebullition occur at a significantly lower frequency than both the bare and willow cores. Over the course of 99 total fluxes, ebullition was only

identified in three fluxes for the sedge cores while the bare and willow cores had 16 and 17 ebullition events occur, respectively. On top of that, the ebullition that did occur was at a significantly lower concentration in the sedge cores than the bare and willow cores. This suggests that vascular plant coverage does have the ability to influence the amount of ebullition that occurs.

There are quite a few reasons as to why these discrepancies exist between each core type. One contributing factor is likely the fact that the sedge cores had a much higher amount of aboveground vascular plant cover than the willow and bare cores. When vascular plant cover was dried and weighed, the sedge cores aboveground biomass was nearly 3.5 times greater than the willow cores, while the bare cores had no vascular plants present. This then led to differences in belowground biomass with the sedge cores likewise having the greatest sum of belowground biomass (1042.27 g m^{-2}) compared to the willow (695.88 g m^{-2}) and bare (187.14 g m^{-2}) cores. Chanton (2005) suggests that an increase in vascular plant cover can lower the pore water CH_4 concentrations, which was seen during this experiment as pore water CH_4 concentrations were significantly greater in the bare and willow cores than the sedge cores for both depths. Strack et al. (2017) also found a similar trend where *C. aquatilis* plots had significantly lower pore water CH_4 concentrations in relation to other plots. Ebullition has also been shown to be greater in open water areas than areas with emergent plants in beaver ponds (Dove et al., 1999). This suggests that an increase in vascular plant coverage will lead to a decline in pore water CH_4 concentration due to increased oxidation and vascular plant transport and thus lower rates of ebullition.

Linear relationships were also observed between belowground biomass and pore water CH_4 concentration. A strong negative correlation (R^2=0.84) was found for roots at 15 cm in depth and pore water at 10 cm while a moderate negative correlation (R^2=0.48) was present between roots at 15-30 cm and pore water at 25 cm. These correlations were likely caused by the increasing amount of vascular plant cover lowering CH_4 concentrations below the surface due to consistent plant-mediated transport of CH_4 (Chanton, 2005) which restricts the formation of ebullition. Additionally, these vascular plants can reduce the effects of methanogenesis by supplying the rhizosphere with oxygen which can promote oxidation of CH_4 (Agethen et al., 2018). This concept has further been exhibited when clipping of vascular plants led to an increase in pore water CH_4 concentrations (Waddington et al., 1996; Strack et al., 2006). Additionally, increases in root coverage can lead to less room for free-phase gas to form. Also, these roots can become quite intertwined and form 'knots' which will further restrict the flow of ebullition throughout the peat profile. This issue was also likely experienced during the field study as the willow area experienced much lower amounts of ebullition compared to the other two locations. More

complex root systems were likely present in the peat which could have prevented the movement of bubbles. This was likely not replicated in the greenhouse experiment for the willow cores as the *Salix* sampled were much smaller in size than the *Salix* that was present in the willow field sampling location.

As mentioned earlier, while a few experiments have been completed to assess the effects of vascular plant coverage on ebullition, each study has rather different findings. Christensen et al. (2003) determined that ebullition can contribute anywhere from 17-52% of total CH_4 emissions depending on the coverage of sedges. Similarly, Ström et al. (2005) saw that *Carex rostrata* contributed about 23% of CH_4 emissions from ebullition while *Eriophorum vaginatum* only contributed 3.5%. While it appears at first that the difference in ebullition might be explained by vascular plant type, the *Eriophorum* monolith had over twice the amount of aboveground biomass than the *Carex* monolith. Similar results were found in this study when the willow cores had 26.1% of CH_4 emissions come from ebullition while only 1.9% came from the sedge cores, which is likely explained by the fact that the sedge cores had over three times as much aboveground biomass. These findings from the greenhouse experiment may seem counterintuitive due to ebullition being the greatest in the sedge location in the field; however, it is important to note again that the overall sedge cover was much lower in the field than in the greenhouse, suggesting the fact that both vegetation type and coverage are important controls of ebullition. Finally, a study by Green and Baird (2012) saw no significant differences in ebullition between cores that had sedges present and not present. However, ebullition contributed only 7% of the total CH_4 emissions from cores with sedge present while their no sedge, moss-dominated cores had ebullition contributing 28% because these cores had lower total CH_4 emissions overall. Based on past results as well as this experiment, there appears to be more of an importance on the amount of vascular plant coverage rather than vascular plants being present for the amount of ebullition that may occur. Throughout this experiment, the total amount of ebullition was quite similar between the bare cores (59.2 mg CH_4 m^{-2}) and the willow cores (53.3 mg CH_4 m^{-2}) despite the presence of vascular plant coverage in one. The importance of considering increased vascular plant cover comes to light when comparing the amount of ebullition from the willow cores and sedge cores (3.0 mg CH_4 m^{-2}). Despite similar vascular plant species in each core, it appears that the abundance of *Carex* greatly diminished ebullition from occurring within the sedge cores. The bare, willow and sedge cores had 46.9, 26.1 and 1.9% of CH_4 emissions be contributed by ebullition, respectively. This has shown that there is a downwards trend as increasing vascular vegetation reduced the contribution of ebullition to overall CH_4 release.

Based on results from this study a conceptual model for plant-soil-hydrology interactions leading to ebullition importance can be developed (Figure 2.11). As vascular plant coverage increases, so do roots and the size of the rhizosphere. This can then lead to an increase in oxygen that is brought into the peat, as well as more efficient transport for CH_4 to the atmosphere. As this occurs, CH_4 pools will decrease and ebullition will become less prevalent. Soil properties such as increasing temperature can also increase ebullition while an increase in bulk density can result in a reduction of ebullition. Meanwhile, sudden decreases in water table levels can reduce hydrostatic pressure, thus increasing ebullition rates. This model can help improve peatland management practices and estimations of CH_4 emissions. Peatlands as a whole, or specific areas of a peatland, that lack vascular vegetation would likely have a larger percentage of total CH_4 emissions come from ebullition. Contrary to that, peatlands that are abundant in vascular vegetation will likely have a lower contribution from ebullition for total CH_4 emissions. It is important to note that these results are from a controlled experiment, and what is happening in the natural world is likely to vary due to changes in hydrological and soil controls as seen from the field data. Additional research is needed to determine how vegetation other than vascular plants (i.e., moss) influence ebullition as well as more studies overall to further our understanding of variables that may enhance or restrict ebullition.

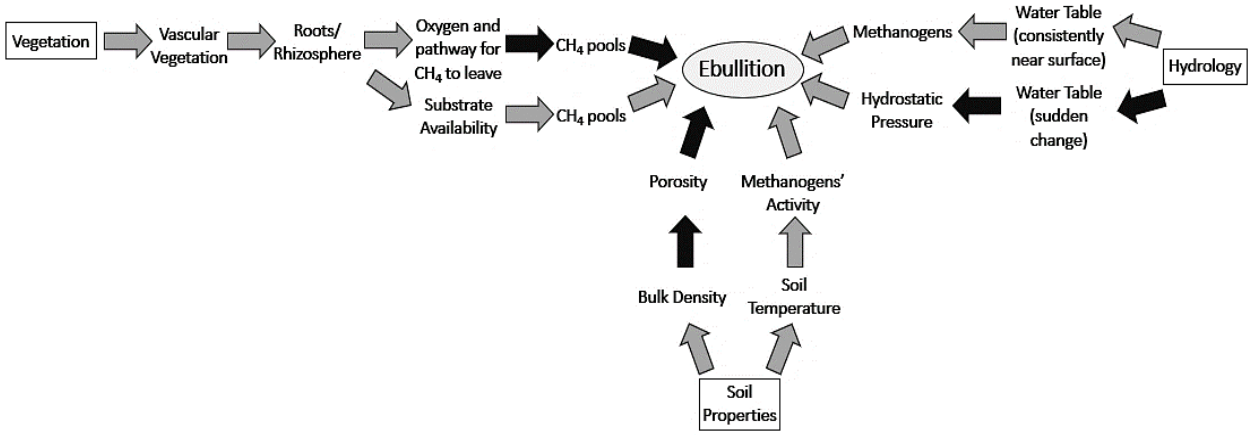

Figure 2.11: Conceptual model for plant-soil-hydrology interactions of ebullition. Grey arrows represent an increase while black arrows represent a decrease.

2.4.3 Importance of Ebullition

While ebullition is often not accounted for when calculating growing season or annual CH_4 emissions, research has shown that ebullition can be an important mechanism for overall CH_4 emissions (Stamp et al., 2013). Stanley et al. (2019) determined that ebullition contributed to over 38% of spring and summer CH_4 emissions in a floodplain fen, while Jeffrey et al. (2019) calculated that ebullition

amounted for 20% of CH_4 released into the atmosphere annually from a subtropical wetland in Australia. These studies have helped demonstrate the importance of ebullition as a pathway for CH_4 release and if disregarded, it could lead to a severe underestimation of total CH_4 emissions. Average steady CH_4 flux measurements from this fen with no consideration of episodic ebullition from June to October was 67.3 mg CH_4 m^{-2} d^{-1} (data from Chapter 3) while average ebullition flux during the same time was 13.2 mg CH_4 m^{-2} d^{-1}. In terms of total amount of CH_4 emitted over this time, steady flux released approximately 10.2 g CH_4 m^{-2} while ebullition released around 2.0 g CH_4 m^{-2}. This means that from June-October, ebullition represented approximately 16.4% of CH_4 that was released into the atmosphere. Moving forward, ebullition should be accounted for when estimating CH_4 emissions for peatland greenhouse gas accounting and management decisions especially at larger scales. While it is difficult to measure, it has been shown in numerous studies to contribute a substantial proportion of total CH_4 emissions.

2.5 Conclusion

Ebullition was found to be quite variable on a spatiotemporal scale. Ebullition fluxes and volume fluctuated not only over time during sampling, but also throughout the fen. In the field, the lowest amount of ebullition consistently occurred in the willow area, while the sedge area had the greatest ebullition release. Water table, soil properties and pore water CH_4 concentrations were important predictors of variation in ebullition amongst locations and increasing soil temperatures likely led to increases in ebullition over the summer period. While consistent decreases in atmospheric pressure sometimes led to an increase in ebullition, measurements at a finer temporal resolution are needed to confirm that atmospheric pressure was the driving factor behind these increases. In the greenhouse experiment, high amounts of vascular vegetation were found to limit the amount of ongoing ebullition by greatly reducing pore water CH_4 concentrations at different depths. This suggests that it is likely that certain peatlands will experience more ebullition than others based on the amount of vascular vegetation that is present, with a threshold of vegetation cover beyond which ebullition is greatly reduced. Over the course of the field sampling period, ebullition fluxes represented 16.4% of the total CH_4 released into the atmosphere. While ebullition rates are sometimes not considered when calculating annual CH_4 emissions, this study demonstrates that ebullition can be a major contributor to the overall release of CH_4, especially during the growing season and even in sites where graminoids form the dominant vegetation cover. Completely ignoring this pathway of release will lead to an underestimation of total CH_4 emissions.

Chapter 3: Determining Interannual Steady Methane Flux Trends and Relationships to Environmental Conditions Within a Calcareous Fen in Southern Ontario

3.1 Introduction

Despite wetlands and peatlands being the world's largest natural source of methane (CH_4) (Fung et al., 1991), which on a 100 year time scale is ~28 times more effective at trapping heat in the atmosphere than carbon dioxide (CO_2) (Stocker et al., 2013), they still remain an essential ecosystem for soil carbon storage, hydrologic regulation and habitat. CH_4 cycling from a peatland can be quite a complex process as it is influenced by many variables. This leads to difficulty in accurately quantifying and upscaling CH_4 emissions, especially when data is often lacking for non-growing season emissions. Due to this, it is necessary to continue research into furthering our understanding of the controls of CH_4 dynamics in peatlands not only during the growing season, but the non-growing season as well to more accurately assess the amount of ongoing carbon sequestration and greenhouse gas exchange for various peatland management strategies, the contribution of peatlands to the global carbon cycle, and how CH_4 emissions might respond to climate change (Moore et al., 1998). To do this, multi-year records of steady CH_4 fluxes (fluxes containing diffusion, plant mediated transport and potentially steady ebullition, excluding episodic ebullition) will be examined to determine how changing environmental variables impact the overall production and release of this greenhouse gas and to identify variables that are the dominant controls of CH_4 fluxes. Additionally, non-growing emissions will be quantified to determine their contribution towards annual emissions.

Peatlands can be excellent at removing atmospheric CO_2 and storing it within their accumulating peat. Conditions that enhance carbon sequestration, such as water-saturated soils, are the same conditions that make peatlands important natural sources of CH_4 (Craft 2015). CH_4 is produced in these ecosystems by methanogenic archaea as a by-product of the decomposition of available organic matter (Jeffrey et al., 2019). Production of CH_4 is typically dominant in the anoxic zones due to do a reduction of available oxygen that can be used to oxidize CH_4 into CO_2 (Whiting and Chanton, 2001). However, research has suggested that methanogenesis can also be present in oxic conditions (Donis et al., 2017) as well as be oxidized in the anoxic zone (Smemo and Yavitt, 2007). CH_4 can leave a peatland's system and enter the atmosphere through three different transportation ways: diffusion, plant mediated transport and ebullition. Diffusion is the movement of CH_4 through the peat up towards the surface to eventually reaching the atmosphere (Walter and Heinmann, 2000). Plant mediated transport occurs when vascular plants have CH_4 from the peat travel through their aerenchyma to reach the atmosphere

(Strack et al., 2006). Finally, ebullition refers to the release of bubbles containing high concentrations of CH_4 to the atmosphere (Coulthard et al., 2009). These events are often episodic which can result in high amounts of CH_4 being released to the atmosphere in a short period of time (Green and Baird, 2012).

The amount of CH_4 that is emitted from a peatland is based on the combination of ongoing production and oxidation of CH_4. When oxygen is available, microorganisms called methanotrophs will consume CH_4 that is available. Environmental factors such as soil temperature, water table and plant productivity have all been shown to influence CH_4 emission in various ways. Soil temperature can influence microbial activity as microbes will become more active in warmer temperatures (Joabsson et al., 1999) leading to an increase in CH_4 production. Strong positive correlations have also been found between average daily CH_4 fluxes and average water table depth, with increasing CH_4 fluxes as the water table nears the surface (Pelletier et al., 2007). Additionally, several studies have found that draining a specific area of a peatland results in lower CH_4 emissions when compared to natural areas (Turetsky et al., 2008; Strack and Waddington, 2007; Ballantyne et al., 2014). These reduced CH_4 fluxes are due to a decrease in the thickness of the anoxic zone, thereby reducing the number of methanogens, while also increasing the number of methanotrophs and oxygen availability. Plant productivity, specifically when vascular plants that are graminoids are present, has been shown at times to have a positive correlation with CH_4 emissions. This is due to productive plants promoting CH_4 transportation through their aerenchyma as well increasing the amount of available labile carbon substrates for methanogenesis from root exudates and litter (Whiting and Chanton, 1993; Waddington et al., 1996). Unlike graminoids, it remains unclear what influence woody plants, such as shrubs, have on peatland CH_4 emissions (Covey et al., 2019). Not only can all these controlling variables change on a year to year basis, they can also fluctuate throughout a peatland resulting in differing CH_4 emissions spatially.

One area of CH_4 flux research that is severely lacking are non-growing season measurements. Non-growing season emissions can be rather difficult to capture due to harsh conditions, especially in areas with long, cold winters. To deal with this omission of data, it is often a common practice to assume that the non-growing season emissions are either 15% of annual emissions (Saarnio et al., 2007) or 15% of the growing season (Webster et al., 2018) when calculating annual CH_4 emissions from a peatland. While this assumption is used, it is highly possible for the growing season of one year to follow a different trend than the non-growing season. If the growing season is warmer and wetter than average this may not necessarily translate to the non-growing season following a similar trend. Considering this, it is possible that using 15% of annual emissions can result in either an under- or overestimation of the

non-growing season flux (Treat et al., 2018). Past studies have shown that non-growing season emissions can vary from this 15% value. For example, Strack et al., (2004) determined that non-growing season CH_4 emissions in some instances were 23.8% of annual emissions in a poor fen near St. Charles-de-Bellechasse, Quebec, Canada. Similarly, Alm et al., (1999) found that winter CH_4 fluxes accounted for 22% of annual emissions from a bog but only 10% from a fen in Finland. On the other hand, Pelletier et al., (2007) observed that non-growing season CH_4 emissions were 13% of annual emissions. These studies demonstrate the fluctuating nature of CH_4 emissions and the potential that these two different seasons have no consistent relationship to one another. Due to such a small sample size of actual non-growing season measurements, it is crucial to further our understandings of peatland CH_4 emissions during this time to better estimate annual emissions.

The purpose of this chapter is to investigate spatial and temporal variability in CH_4 emissions within a southern Ontario calcareous fen. The main objectives were to: (1) Compare growing season and non-growing steady CH_4 fluxes across a four-year period (2016-2019) to identify flux trends throughout each type of season as well determine if any relationship exists between the two different seasons. (2) Compare steady CH_4 fluxes spatially within the fen to identify any spatial variability as well as to determine if the presence of the shrub *Salix* (willow) has any influence on overall CH_4 emissions. (3) Investigate environmental variables (water table, soil temperature, pore water CH_4 concentration and vegetation productivity) to see how relationships to CH_4 emission differed between the different sampling locations.

3.2 Methods

3.2.1 Study Site

Research was conducted in a natural calcareous fen located in the township of Puslinch, which is approximately 20 km south of Guelph, Ontario, Canada. This fen is established in Fletcher Creek Ecological Preserve (43°24’55.422” N, 80°7’0.3612” W) and is part of the Spencer Creek Watershed. A main river flows through the middle of this peatland that is contributed to by a small tributary stream. Due to local topography, water pools in the southern portion of the fen resulting in frequent inundation. The vegetation is primarily dominated by graminoids such as *Carex* spp. but also contains shrubs which are sparsely distributed throughout. A cedar forest surrounds the fen and landcover outside of the ecological preserve is agricultural land and rural homes.

Six metal collars were inserted ~15-25 cm into the peat in 2016 to capture and measure greenhouse gas exchange. Three of these collars were installed just north of an area of water pooling

within the fen (FL4-6, referred to as the 'sedge' area) while the other three were installed ~15 m east near a small tributary stream (FL0-3, referred to as the 'stream' area). Two additional collars (FL0 in the stream area, FL7 in the sedge area), one at each location, were installed before the growing season of 2017. Each collar installed at this time consisted heavily of *Carex*. In April 2019, four new collars (FL8-12) were installed in areas that had a mix of both *Carex* as well as *Salix*. This was done in an area ~8 m north of the stream area (referred to as the 'willow' area). These collars were installed to determine if the presence of *Salix* influenced steady CH_4 flux in any way.

3.2.2 Defining the Growing Season and Non-growing Season

Using a growing season length map of Canada, it was determined, based on geographical location, that this fen had a growing season that lasted between 141 and 160 days (Natural Resource Canada, 2020). This was calculated by the total number of days between the last occurrence of 0 °C in the spring and the first occurrence in the fall (Natural Resource Canada, 2020). With these criteria in mind, a weather station ~25 km north of the fen (Guelph Turfgrass; 43°33'00.000" N, 80°13'00.000" W) was used to view temperature data for the past 10 years. When viewing minimum temperatures, it appeared that the last occurrence of 0 °C in the spring was typically around the end of April while the first occurrence in fall was around the beginning of October. Based on this information, it was decided to assign the growing season for this study from May 1st to September 30th, equalling 153 days total. Therefore, the non-growing season would be October 1st to April 30th for a total of 212 days. Linear interpolation was used to determine growing season and non-growing season CH_4 fluxes. This was calculated by determining an integrated flux of CH_4 between a pair of samples at two consecutive measurement dates (Baird et al., 2019). The following equation from Baird et al. (2019) was used:

$$F_{g,1-2} = \frac{1}{2}(f_{g,1} + f_{g,2})(t_2 - t_1)$$

where f_g is the measured instantaneous flux on a given day and t is equal to the day of the year. Afterwards, $F_{g,}$ values can be summed for either a seasonal or annual total (Baird et al., 2019). Since a good data set exists for only up until December for all four years, non-growing season fluxes were calculated only up until that day, representing the period of October 1st to December 31st (92 days). Values from this period can also be extended to the entire non-growing season; however, it is important to note that doing so will leave uncertainty as very few values were collected during the January – April time period and it would be based on the assumption that fluxes were similar to the earlier non-growing season period.

3.2.3 Methane Fluxes

Methane flux was measured with the static closed chamber method (Alm et al., 2007) from the years 2016-2019. Bi-weekly measurements were made from May-December for the years 2016-2018. However, in 2019, weekly measurements were made from May-August but were switched back to bi-weekly measurements from September to December. To correct for volume of the headspace, the depths of each individual collar were measured from the top of the collar down to the soil surface at 12 random locations within each collar and averaged as the topography in each collar varies. In the instance that standing water was above a collar, the amount of headspace that was between the top of the chamber when on the collar and the water surface was measured and corrected for accordingly.

Opaque chambers (60 cm $\times$ 60 cm $\times$ 30 cm) were placed on each collar to measure CH_4 flux. If the collar was not submerged underwater, water was poured around the edge of each collar to ensure that there was an airtight seal between the collar and chamber. In one instance, during the non-growing season, a layer of ice had completely covered each collar. To deal with this, the chambers were placed on the ice above each collar and snow was tightly packed around the chamber to create a seal. A battery powered fan was also placed in each chamber to promote air circulation. A hole was located at the top of the chamber and was left open during chamber placement to avoid overpressuring and then was plugged as flux measurements began. Connected to the plug was thermocouple wire to record chamber temperature at the time of sample collection as well as Tygon tubing attached to a three-way valve and a 20 mL syringe. For the years 2016, 2017 and a quarter of 2018, gas samples were taken at 7, 15, 25 and 35 minute after chamber closure while the rest of 2018 and all of 2019 was sampled using a 5, 10, 15 and 20 minute time steps. There was a switch to shorter time intervals due to consistently high amounts of CH_4 being emitted from this fen, so it was not required to wait as long to see linear trends develop. To determine if flux rates from 2016 – 2018 would be similar with this shorter sampling interval, calculated fluxes that used the entire 35 minutes were compared to the same fluxes but only calculated up until the 25-minute interval. These results showed that the difference in fluxes were typically around ±5-10% of mean study flux for the year indicating that both time frames produce similar results. Prior to a gas sample being collected, the 20 mL syringe was pumped for 30 seconds to promote air circulation and movement within the chamber and tubing. Then 20 mL of air from within the chamber was pulled into the syringe and immediately injected into an evacuated vial (12 mL Exetainer, Labco Ltd, UK). Once the samples were collected, a gas chromatograph (GC, Shimadzu GC2014) with a flame ionization detector was used to determine the concentration of CH_4 in each sample.

To calculate daily flux rates, linear changes in CH_4 concentrations over time were calculated. Chamber head space and temperature were adjusted for each flux calculation. Data was quality controlled based on the R^2 value and change in concentration. Any flux measurement with a slope that had an R^2 value less than 0.75 was omitted as this suggests that the concentration change was not linear. If a flux slope had an R^2 value of 0.75 or greater but the difference in CH_4 concentration from the first and last sample was less than the precision of the measurement from the gas chromatograph which is 0.5 ppm, the flux was assigned a value of 0. Additionally, if the initial 5-minute sample of a flux measurement had a CH_4 concentration of 5 ppm or greater and then saw a gradual decrease over time, this data was also removed as it is likely that a human-induced ebullition event occurred when putting the chamber on the collar. In certain instances, flux measurements captured natural episodic ebullition events. This resulted in those specific flux measurements to be often an order of magnitude higher than a traditional steady flux (diffusion and plant mediated transport), which can severely skew statistical results. Additionally, because episodic ebullition events are so random in nature, by chance it is possible to capture more of these events during chamber fluxes in one year than another even though the overall contribution of ebullition could be less. Due to these reasons, it was decided to remove any flux measurements that contained episodic ebullition and statistical results and averages are based solely on steady flux rates. A flux was deemed to contain episodic ebullition if the CH_4 concentration between two consecutive intervals were doubled or more in comparison to the other intervals. To accurately assess the amount of CH_4 emitted by ebullition, it is required to measure the process on its own. Furthermore, the number of these instances are quite small for each year, 5 being the greatest in 2019 and 0 being the lowest in 2018. Even though ebullition was not present in any chamber fluxes in 2018, that does not mean that ebullition was not occurring during that year. While fluxes containing ebullition are excluded for statistical analysis, it is still accounted for in the calculations of annual CH_4 emissions in 2019 when ebullition was measured separately with funnel traps (Chapter 2). In the end, 78, 81, 87 and 82% of flux measurements were kept in the analysis for the years 2016-2019, respectively.

3.2.4 Pore Water Methane Concentration

Pore water samples were collected adjacent to each collar in 2019 and were later analyzed for CH_4 concentrations. These samples were collected at two depths for each collar, 15 and 40 cm below the surface. This was done to gain a greater spatial understanding of the subsurface CH_4 pools that exist throughout the fen. Pore water samplers were made by cutting 2.54 cm inner diameter PVC pipe into 20 cm lengths. Then from 5-15 cm, holes were drilled into the PVC pipe and then covered by 250 µm Nitex

screening to help prevent clogging and potential peat build up in the pore water sampler. A cap was placed at both ends of the PVC and a hole was drilled into one to allow Tygon tubing to be placed inside the PVC pipe (Mahmood & Strack, 2011). The tubing was long enough to extend to the surface where a three-way valve was attached at the end. These pore water samplers were then inserted into the peat so that the middle of the sampler would be at the depths of 15 cm and 40 cm below the ground surface by using an auger. To collect samples, a 60 mL syringe was attached to the three-way valve and used to draw up water from below the surface. First water in the tubing was purged and used to rinse the syringe, and then another 20 mL water sample was taken. Once 20 mL of water was collected, 20 mL of ambient air was added to the syringe. Afterwards, the syringes were shaken for 5 minutes to transfer the dissolved gases from the water into the air. Once shaking was complete, the air within the syringe was transferred into an evacuated Exetainer and later analyzed on the GC. Dissolved CH_4 concentration was calculated based on the measured headspace concentration and the air temperature at the time the samples were collected (Strack et al., 2004; Kampbell and Vandegrift, 1998). This sampling took place whenever CH_4 steady flux measurements were made.

3.2.5 Environmental Variables

When CH_4 flux measurements were collected, soil temperature was recorded adjacent to each collar using a soil thermocouple temperature probe. Soil temperatures were taken at depths of 2, 5, 10, 15, 25 and 30 cm. Additionally, water table was recorded on the same time scale at each of the three central fluxing locations. This was accomplished by installing a long piece of PVC with drilled holes along its length into the peat. To determine water table levels, a blow pipe with a measuring tape was used to first measure the length of the PVC pipe that was above the surface. Then, the blow pipe was inserted into the PVC pipe and blown into until the sounds of bubbles were heard where another measurement from this location was recorded at the top of the PVC pipe to determine how far down the water level was in the PVC pipe. Afterwards, outside length was subtracted from the inside length to calculate the water table level at the specific location.

Productivity of the plants located in each collar was measured in each study year to determine if any relationships existed between plant productivity and CH_4 fluxes. To do this, CO_2 exchange was measured on the same days as CH_4 flux measurements were collected. Net ecosystem exchange (NEE) was measured in the field using a transparent dynamic chamber connected to an infrared gas analyzer (IRGA; EGM-4, PPSystems, Massachusetts, USA) under full sunlight to observe and changes in CO_2 concentrations within the chamber were recorded over a 105 second time period. To calculate the gross

ecosystem production (GEP) of each collar, ecosystem respiration (ER) rates were needed as GEP is the difference between ER and NEE. To calculate this, an opaque tarp was placed over the chamber and once again the changes in CO_2 concentrations within the chamber were recorded over a 105 second time period. Similar to the calculation for CH_4 flux, chamber headspace volume and temperature were corrected for when calculating GEP. For the purpose of this study, negative GEP values will represent an uptake of CO_2 (plants being more productive). For the months of June and July in 2017, no temperature was recorded during CO_2 measurements due to a broken thermocouple wire. To correct this, the 7-minute time interval temperature that was recorded during the CH_4 measurements on the corresponding day was applied to the CO_2 chamber temperature. Also, CO_2 measurements were not taken in late November and December in 2018. For these sampling days, GEP was assumed to be zero due to the plants likely not being active at this time of year. In addition, CO_2 measurements were no longer collected from mid-November and onwards in 2019 due to colder weather causing the IRGA not to work. However, GEP measurements leading up to this time were nearly 0 confirming the fact that the plants were seldomly active, so a GEP value of 0 was assumed for all collars at this time.

Vegetation cover in each plot was visually estimated on August 14th, 2019 to determine overall vegetation coverage and type within each collar. Due to the difficulty to determine different *Carex* species within this fen without destructive sampling, live vegetation was identified to the genus level with an estimated canopy cover.

3.2.6 Statistical Analysis

Due to repeated measurements in the same locations over the course of a few years, linear mixed effects (LME) models were used in R (R Core Team 2019) with collar being set as a random factor using the nlme package (Pinheiro et al., 2018). Every model was visually inspected for normality and homogeneity of residuals and if needed, data was transformed (Zuur et al., 2009). A statistical significance level of $\alpha = 0.05$ was used for all tests. Growing season CH_4 emission data was log transformed with a value of one added as some measurements were 0. Additionally, non-growing season CH_4 emissions were log transformed with an added value of 20 due to negative fluxes being present. Growing season and non-growing season were not compared statistically except for in 2019 when both seasons were log transformed with an addition of one.

Environmental variables, which included soil temperature, pore water CH_4 concentrations, water table and GEP were tested for significant differences among years and locations by using a one-way ANOVA. In order to compare growing season and non-growing season CH_4 fluxes among years, an

LME model was used assigning year as a fixed factor and collar as a random factor. When significant differences were found, a Tukey pairwise comparison was used to determine where the differences exist among years. This was completed by using the multcomp package available in R (Hothorn et al., 2008). The same steps and procedures were used for comparing CH_4 fluxes among locations for the year 2019. All statistical F-values that are reported in this study was obtained using the ANOVA command in R.

To investigate significant controls of CH_4 fluxes in 2019, when fluxes were collected at a higher temporal resolution, and whether these varied between each collar grouping, a complete LME model was initially constructed containing soil temperature at 15 and 30 cm, water table level, GEP, and pore water CH_4 concentration at 15 and 40 cm depths as fixed factors. Two-way interactions between each variable were also included in the initial model with collar as a random factor. Once the initial model was constructed and then run for the entire data set as well as location specific data, non-significant factors were removed one at a time, starting with the highest p-value. However, if a variable was not considered significant on its own but was significant within an interaction that individual variable was kept in the model. A small amount of heterogeneity was detected in the model assessing the influence of variables amongst all locations together, as well as for the willow location individually. A varIdent variance structure was applied with different variance by collar for the model that involved measurements from all areas, while a variance structure by month was applied for the willow location model, which improved overall normality and homogeneity of residuals. Furthermore, R^2 values have been provided for LME models and were obtained through the MuMIn package (Barton, 2018).

3.3 Results

After data quality checks were complete and poor-quality data was removed, 41, 52, 67 and 138 individual CH_4 flux measurements were included for the growing season in 2016, 2017, 2018 and 2019, respectively. Since 2019 had such a larger sample size compared to the other years due to sampling on a weekly time scale, bi-weekly measurements were tested during statistical analysis to ensure that the higher resolution sampling did not introduce bias. However, results remained the same, thus the data set for 2019 includes weekly measurements. In 2019, four additional collars that contained *Salix* were installed to further investigate spatial variability. As these were not present in the data sets from previous years, these collars were not included in the analysis of interannual variability in steady CH_4 flux. When it comes to the non-growing season, 25, 39, 37, and 38 individual steady CH_4 flux measurements were included in 2016, 2017, 2018 and 2019, respectively. For comparing CH_4 fluxes between locations during the growing season in 2019, the sedge location had a total of 78 fluxes, the

stream had 60 while the willow location had 73. Total non-growing season measurements were 22, 17 and 20, respectively for each area.

3.3.1 Vegetation Survey

Carex spp. was the most dominant vegetation across all collars (Table 3.1). Additionally, graminoids made up the majority of the plant cover in every collar except for FL10, which had 70% cover of *Salix petiolaris.* FL6 had the highest graminoid coverage of 58% while FL10 had the least with a percentage coverage of only 15%. No moss was present in any location. Also, shrubs were only present in the 'willow' grouping of collars while various forbs were found throughout the collars.

3.3.2 Interannual Variation in Methane Flux

3.3.2.1 Environmental Variables

When comparing growing season environmental variables across all years, average soil temperature at 15 cm was the greatest in 2016 (16.9 °C) and followed a downward trend to 2019 (15.4 °C), but no significant differences were found ($F_{3,285}$=2.5, p=0.0564). The same trend was found for soil temperature at 30 cm (Table 3.2); however, in this case there was a significant difference between 2016 and 2019 ($F_{3,285}$=4.7, p=0.0024). For water table, there was a fluctuation between the average water table being below the surface and then above. The year 2018 had the lowest average water table level at -7.0 cm while 2017 had the greatest at 8.2 cm. Both 2017 and 2019 water table levels were found to be significantly higher than all other years ($F_{3,287}$=46.5, p<0.0001). Overall, 2016 had a water table range of -20 to 15 cm, and 66% of fluxes were taken when the water table was below the surface. In 2017, the range was from -9.5 to 17 cm while only 12% of fluxes were taken when the water table was less than 0 cm. On the other hand, 2018 had 84% of flux measurements taken when the water table was below the surface with a range of -18 to 8 cm. Finally, 2019's water table ranged between -15 and 20 cm during sampling with 40% of fluxes having a water table below the surface. Plant productivity was the greatest during the 2018 growing season (-20.3 g CO_2 m^{-2} d^{-1}) and was the lowest in 2017 (-18.3 g CO_2 m^{-2} d^{-1}) with no significant differences between years ($F_{3,266}$=0.6, p=0.616).

Table 3.1: Vegetation survey of each individual collar that was used for CH_4 fluxes. Due to the time of year that this vegetation survey was completed it was difficult to correctly identify certain vegetation to the species level, thus some vegetation was only identified to a genus level.

Collar	Vegetation Coverage (%)									Bare (%)	Litter (%)	Graminoid (%)	Shrub (%)	Forb (%)
	Carex sp.	*Salix petiolaris*	*Salix candida*	*Muhlenbergia glomerata*	*Galium trifidum*	*Cicuta culbifera*	*Epilobium palustre*	*Lycopus uniflorus*	*Campanula sp.*					
FL0	30			3						15	85	33	0	0
FL1	45			10	5	1					100	55	0	6
FL2	20			5	3		Present	1		10	90	25	0	5
FL3	15			1	3						100	16	0	3
FL4	35			5							100	40	0	0
FL5	20			Present						20	80	20	0	0
FL6	55			3	Present						100	58	0	0
FL7	17			1						2	98	18	0	0
FL8	20	15		5			1				100	25	15	1
FL9	35	30	Present	1	Present						100	36	30	1
FL10	15	70					3				40	15	70	3
FL11	35	25		1					1	2	98	35	25	1

Table 3.2 Summary of environmental variables throughout the four year sampling period for the growing season (May 1-September 30) and non-growing season (October 1-December 31). All values represent an average while values in the brackets are the standard error. Different letters represent a significant difference between years within the corresponding season but should not be compared between seasons.

Year	Season	Soil Temp (°C) 15 cm	Soil Temp (°C) 30 cm	Water Table level (cm)	GEP ($g\ CO_2\ m^{-2}\ d^{-1}$)
2016	Growing	16.9 (0.61)[a]	16.0 (0.58)[a]	-4.1 (1.08)[a]	-18.7 (1.17)[a]
	Non-growing	8.4 (0.72)[a]	9.1 (0.53)[a]	1.8 (1.69)[a]	-7.9 (1.49)[a]
2017	Growing	16.4 (0.40)[a]	14.9 (0.37)[ab]	8.2 (0.91)[b]	-18.3 (1.08)[a]
	Non-growing	7.4 (0.48)[a]	8.6 (0.49)[a]	0.1 (1.20)[a]	-5.6 (1.07)[ab]
2018	Growing	15.9 (0.41)[a]	14.9 (0.41)[ab]	-7.0 (0.83)[a]	-20.3 (1.02)[a]
	Non-growing	6.7 (0.85)[a]	7.6 (0.68)[a]	-1.4 (1.16)[a]	-3.8 (1.02)[b]
2019	Growing	15.4 (0.28)[a]	14.0 (0.26)[b]	3.4 (0.65)[c]	-19.6 (0.73)[a]
	Non-growing	6.2 (0.64)[a]	7.2 (0.59)[a]	-2.6 (0.66)[a]	-3.4 (0.74)[b]

Non-growing season soil temperatures followed a similar trend to growing season soil temperature. Soil temperature at 15 cm was greatest in 2016 (8.4 °C) and the lowest in 2019 (6.2 °C); however, no significant differences were found ($F_{3,132}$=1.8, p=0.144). Soil temperature at 30 cm was the warmest in 2016 (9.1 °C) and the coolest in 2019 (7.2 °C) ($F_{3,131}$=2.3 p=0.0757). Regarding water table, 2016 had the highest average non-growing season water table level (1.8 cm) while 2019 had the lowest (-2.6 cm). However, no significant differences were found ($F_{3,117}$=2.4, p=0.0673). Plants were most productive in the non-growing season during the year 2016 (-7.9 g CO_2 m^{-2} d^{-1}) and least productive in 2019 (-3.4 g CO_2 m^{-2} d^{-1}). Plants were significantly more productive in 2016 compared to 2018 and 2019 ($F_{3,127}$=3.4, p=0.0195).

3.3.2.2 Methane Fluxes

For the growing season, steady CH_4 fluxes were significantly different among years ($F_{3,287}$=37.3, p<0.0001). The lowest average steady flux of 28.5 mg CH_4 m^{-2} d^{-1} was observed in 2018, with a range of 0-222.5 mg CH_4 m^{-2} d^{-1}, and was significantly lower than every other year. On the contrary, in 2017, which had the highest average steady flux of 202.7 mg CH_4 m^{-2} d^{-1} and a range of 0-920.0 mg CH_4 m^{-2} d^{-1}, flux was significantly higher than every other year, while no significant difference was found between the years 2016 and 2019 ($F_{3,287}$=37.3, p=0.0538). In 2016, the average steady flux was 55.3 with an overall range of 0-306.7 mg CH_4 m^{-2} d^{-1} and 2019's steady flux average was 73.2 mg CH_4 m^{-2} d^{-1} with fluxes that ranged from 0-396.23 mg CH_4 m^{-2} d^{-1}. These fluxes are shown in Figure 3.1.

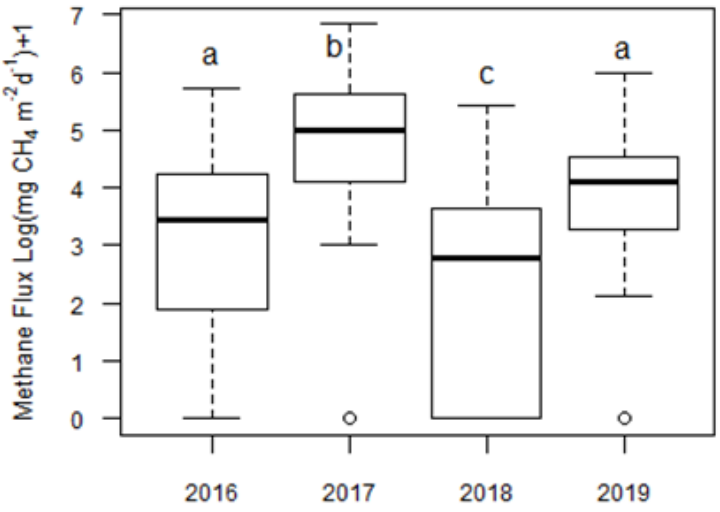

Figure 3.1: Boxplots displaying growing season (May-September) steady CH_4 fluxes that were log transformed for the years 2016-2019. Different letters represent a significant difference between the respective years.

For the non-growing season (Figure 3.2), steady CH_4 fluxes were significantly different between the years 2017 and 2018 ($F_{3,130}$=4.645, p=0.0024), as well as 2018 and 2019 ($F_{3,130}$=4.645, p=0.0427). Average steady CH_4 fluxes were the highest in 2017 with a rate of 30.7 mg CH_4 m^{-2} d^{-1}. The year 2018 had the lowest average steady CH_4 flux of 17.4 mg CH_4 m^{-2} d^{-1}. The non-growing season CH_4 fluxes were overall much less variable than growing season fluxes with averages being more similar across the years.

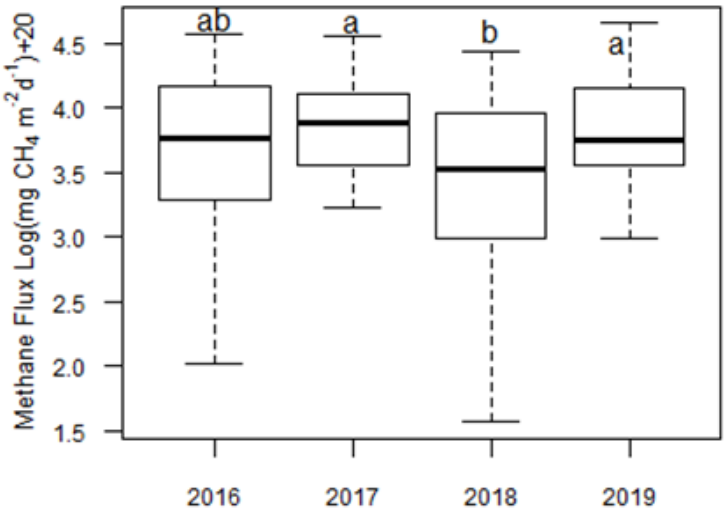

Figure 3.2: Comparison of steady CH_4 fluxes in the non-growing season (October-December) for all four years. Different letters identify a significant difference.

Total CH_4 emitted during the growing season (May 1st – September 30th) through steady flux was 9.4, 30.6, 4.2, and 11.7 g CH_4 m^{-2} for the years 2016-2019, respectively (Table 3.3). Meanwhile, total CH_4

emitted during the same years in the non-growing season (October 1st – December 31st) through steady flux was 2.4, 2.4, 1.7, 2.6 g CH_4 m^{-2}. The percentage of non-growing season steady flux emissions in relation to the growing season was the highest in 2018 with a rate of 41.0% while 2017 had the lowest with 7.8%. Meanwhile the years 2016 and 2019 had a respective total percentage of 25.7 and 21.9%. In relation to other years, the growing season of 2017 emitted at least nearly three times as much CH_4. However, non-growing season emissions for 2017 were quite similar to other years except for 2018. This resulted in non-growing season emissions representing a much smaller portion of overall CH_4 emitted from May-December. It is important to emphasise that these values are based on steady CH_4 flux and excluded the contribution of ebullition. If ebullition was accounted for, growing season totals would rise at a greater rate than the non-growing season, resulting in the non-growing season representing a smaller percentage.

Table 3.3: Growing season and now-growing season steady CH_4 fluxes.

Year	Average CH_4 flux (mg CH_4 m^{-2} d^{-1})		Total CH_4 Emitted (g CH_4 m^{-2})		Non-growing Season Emissions % of Growing Season Emissions
	Growing Season (May 1 to Sept. 30)	Non-growing Season (Oct. 1 to Dec. 31)	Growing Season (May 1 to Sept. 30)	Non-growing Season (Oct. 1 to Dec. 31)	
2016	55.3 (11.08)[a]	26.1 (4.88)[ab]	9.4	2.4	25.7
2017	202.7 (27.33)[b]	30.7 (2.84)[a]	30.6	2.4	7.8
2018	28.5 (4.98)[c]	17.4 (3.71)[b]	4.2	1.7	41.0
2019	73.2 (5.81)[a]	28.4 (3.71)[a]	11.7	2.6	21.9

3.3.3 Spatial Variation in Methane Flux in 2019

3.3.3.1 Methane Fluxes

Comparing steady CH_4 fluxes in the growing season for the year 2019 between groupings found that the sedge location has significantly higher fluxes than the willow location (Figure 3.3; $F_{2,9}$=5.2, p=0.035). Average growing season steady fluxes were 95.7, 45.3 and 44.2 mg CH_4 m^{-2} d^{-1} for the sedge, stream and willow location, respectively. For the non-growing season, no significant differences were found among locations ($F_{2,9}$=0.32, p=0.7318). The average CH_4 flux for the non-growing season in the sedge, stream and willow location were 33.0, 26.2 and 24.5 mg CH_4 m^{-2} d^{-1}, respectively.

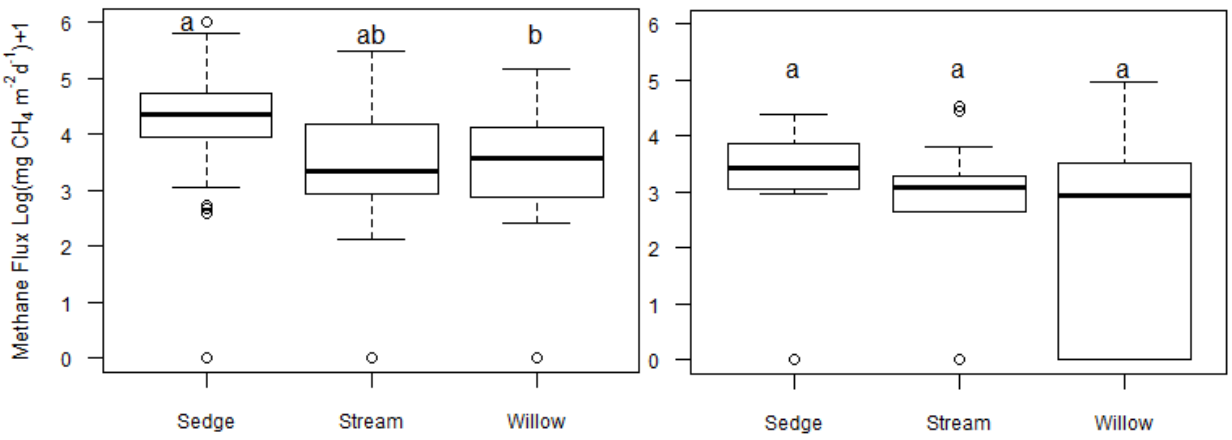

Figure 3.3: Comparison of growing season (on left) and non-growing season (on right) steady CH_4 fluxes for the three different collar groupings. Differing letters represents a significant difference between sections but should not be compared between seasons.

Steady average CH_4 fluxes for each sampling day varied over the course of the growing season with single day measurements typically peaking in July and August for each location (Figure 3.4). For the sedge location, the single highest average of steady CH_4 fluxes from a sampling day was 221.8 mg CH_4 m^{-2} d^{-1} which occurred on July 31st. The willow location also experienced its highest average steady flux during that day at a rate of 101.9 mg CH_4 m^{-2} d^{-1}. Meanwhile, the stream location peaked on August 22nd with a rate of 90.5 mg CH_4 m^{-2} d^{-1}. The lowest daily steady flux for the sedge location occurred on the first day of sampling on May 10th with an average flux of 14.0 mg CH_4 m^{-2} d^{-1}. Both the stream and willow locations experienced a day of measurements where steady CH_4 fluxes were not recorded (i.e., all were below detection limit; this is based off one plot measurement for the stream as the other three were removed due to poor quality of data) and this occurred on June 14th and July 9th, respectively.

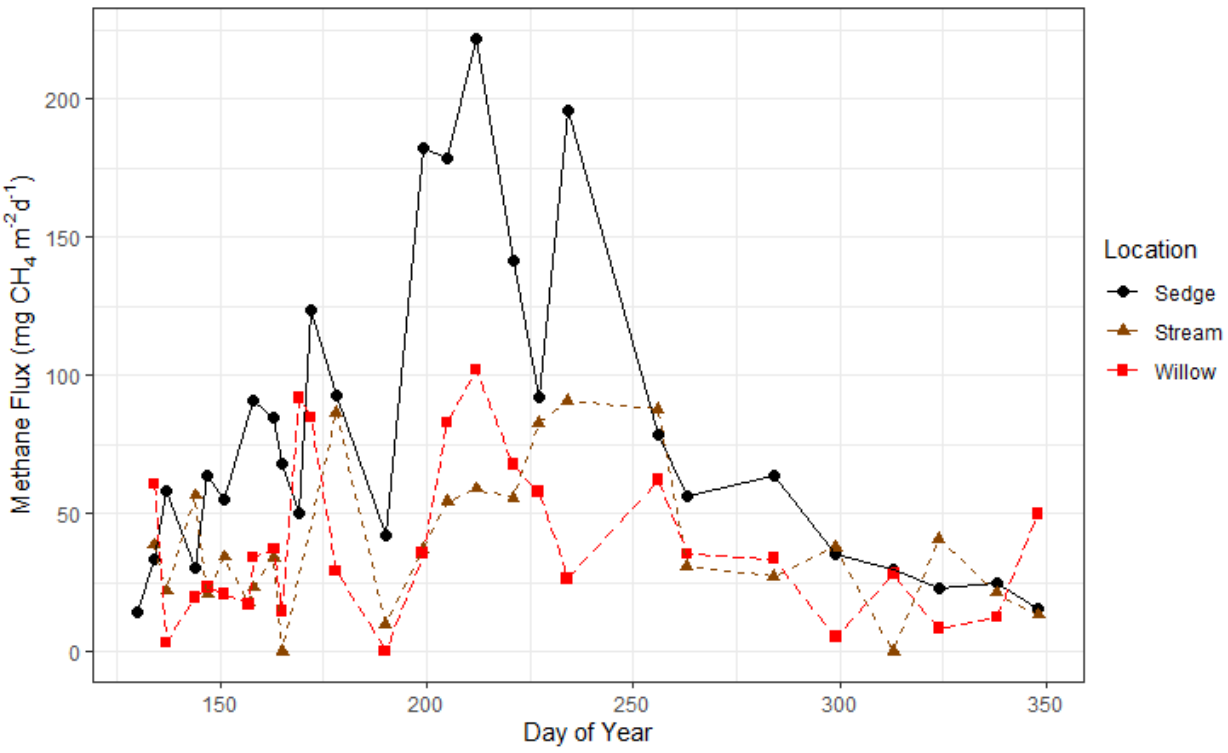

Figure 3.4: Time series graph of average steady CH_4 fluxes for each day of sampling at each location.

When comparing all fluxes amongst months in the growing season (Figure 3.5), there was a significant difference between the months May and August ($F_{4,195}$=5.0, p=0.0005). Average steady CH_4 fluxes increased from May until August, and then decreased in the month of September. The average steady CH_4 fluxes for each month were 34.7, 60.5, 86.2, 100.9 and 56.6 mg CH_4 m^{-2} d^{-1} from May-September, respectively. For the non-growing season, a decreasing trend continued as October, November and December each had consecutive lower fluxes. The average steady flux for these months were 34.8, 29.9 and 24.8 mg CH_4 m^{-2} d^{-1}, respectively. No significant differences were found between the three non-growing season months ($F_{2,46}$=1.4, p=0.2551); however, the month of October was statistically similar to the months May-September.

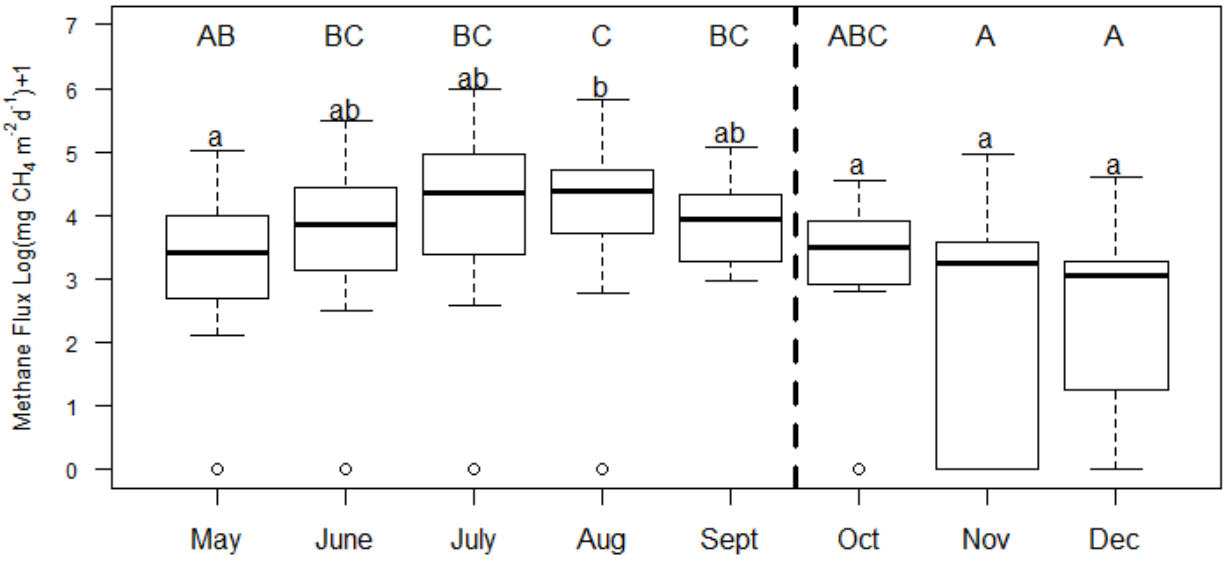

Figure 3.5: Monthly comparison of steady CH_4 fluxes from all sampling locations. Differing lowercase letters identify a significant difference between months in each respective season, which is separated by the dashed line. Differing capital letters means a significant difference between any month while disregarding the season.

3.3.3.2 Annual Methane Emissions For 2019/2020

Previous growing season and non-growing season emissions that were calculated contained only steady CH_4 fluxes while omitting ebullition. However, ebullition was measured and quantified over the course of the growing season in 2019 (Chapter 2) as well as one non-growing season month (October) so it is possible to add its contribution to produce a more accurate estimation of CH_4 emissions for this year. Additionally, the non-growing season can be extended and calculated to its full extend by making assumptions for the months where no data was collected. Flux measurements were collected in January 2020 and will be averaged and applied to February as those months are similar climate wise. The month of April's emissions will be assumed to be 35% of the average May emissions across the four years based on the fact that April 2017 fluxes were ~35% of May 2017. Meanwhile, the month of March will be assumed to be 20% of average total emissions from May. Based on these assumptions, the addition of ebullition, as well as incorporating the willow collars into overall emissions, the new growing season total for CH_4 emissions are 12.0 g CH_4 m^{-2} while the entirety of the non-growing season is 4.0 g CH_4 m^{-2}. Non-growing season CH_4 emissions in 2019 were 33.3% of growing season emissions and accounted for 25.0% of annual emissions.

3.3.3.3 Environmental Variables

Comparing collar groupings during the growing season in 2019, soil temperature at 15 cm was the highest in the stream location (15.7 °C) and the lowest in the sedge location (15.2 °C) but there were

no significant differences between locations ($F_{2,9}$=0.6, p=0.5852). Temperature at 30 cm depth had a similar pattern (Table 3.4), although the stream had the warmest average (14.4 °C) while sedge was the coolest (13.7 °C) ($F_{2,9}$=0.8, p=0.4805). A moderately strong positive correlation was found between both soil temperature at 15 and 30 cm and log CH_4 fluxes (Figure 3.6) for the sedge location (R^2=0.52, 0.47). However, much weaker positive trends were found for the stream location (R^2=0.09, 0.09) and the willow area (R^2=0.15, 0.2). Water table levels were significantly higher in the sedge area (4.4 cm) when compared to the willow area (-1.2 cm) ($F_{2,9}$=7.8, p=0.0108). Overall, throughout the fen water table levels ranged from -16.5 to 20 cm over the course of the growing season. Additionally, a moderately strong unimodal correlation (R^2=0.46 for sedge, R^2= 0.58 for stream, R^2=0.4 for willow) was found among each location between log CH_4 fluxes and water table level with CH_4 fluxes typically peaking when the water table was slightly above the surface level (Figure 3.6). For GEP, the willow collars were significantly more productive than both the sedge and stream collars ($F_{2,9}$=33.0, p<0.0001). Regarding pore water CH_4 concentration at 15 cm, the sedge location (2.73 mg/L) was significantly higher than the stream (0.68 mg/L) and willow (1.09 mg/L) locations ($F_{2,9}$=33.4, p<0.0001). Pore water concentration at 40 cm had a different trend with the willow area having the greatest average concentration (2.48 mg/L); however, no significant differences were found between locations ($F_{2,9}$=2.1, p=0.1805).

Table 3.4: Summary table of potential CH_4-influencing variables for the growing season (May-September). All values represent an average across this sampling period. Differing letters represent significant differences among locations. Values within brackets represent standard error.

Collar Grouping	CH_4 Flux (mg CH_4 m^{-2} d^{-1})	Soil Temp (°C) 15 cm	Soil Temp (°C) 30 cm	Water table level (cm)	GEP (g CO_2 m^{-2} d^{-1})	CH_4 Pore Water 15 cm (mg/L)	CH_4 Pore Water 40 cm (mg/L)
Sedge	94.7 (8.45)^{a}	15.2 (0.38)^{a}	13.7 (0.35)^{a}	4.4 (0.82)^{a}	-19.8 (1.04)^{a}	2.73 (0.17)^{a}	2.24 (0.12)^{a}
Stream	45.3 (11.42)^{ab}	15.7 (0.39)^{a}	14.4 (0.37)^{a}	2.1 (1.34)^{ab}	-19.3 (1.06)^{a}	0.68 (0.10)^{b}	1.65 (0.14)^{a}
Willow	44.2 (7.5)^{b}	15.5 (0.37)^{a}	14.1 (0.36)^{a}	-1.2 (0.91)^{b}	-35.5 (1.96)^{b}	1.09 (0.10)^{b}	2.48 (0.19)^{a}

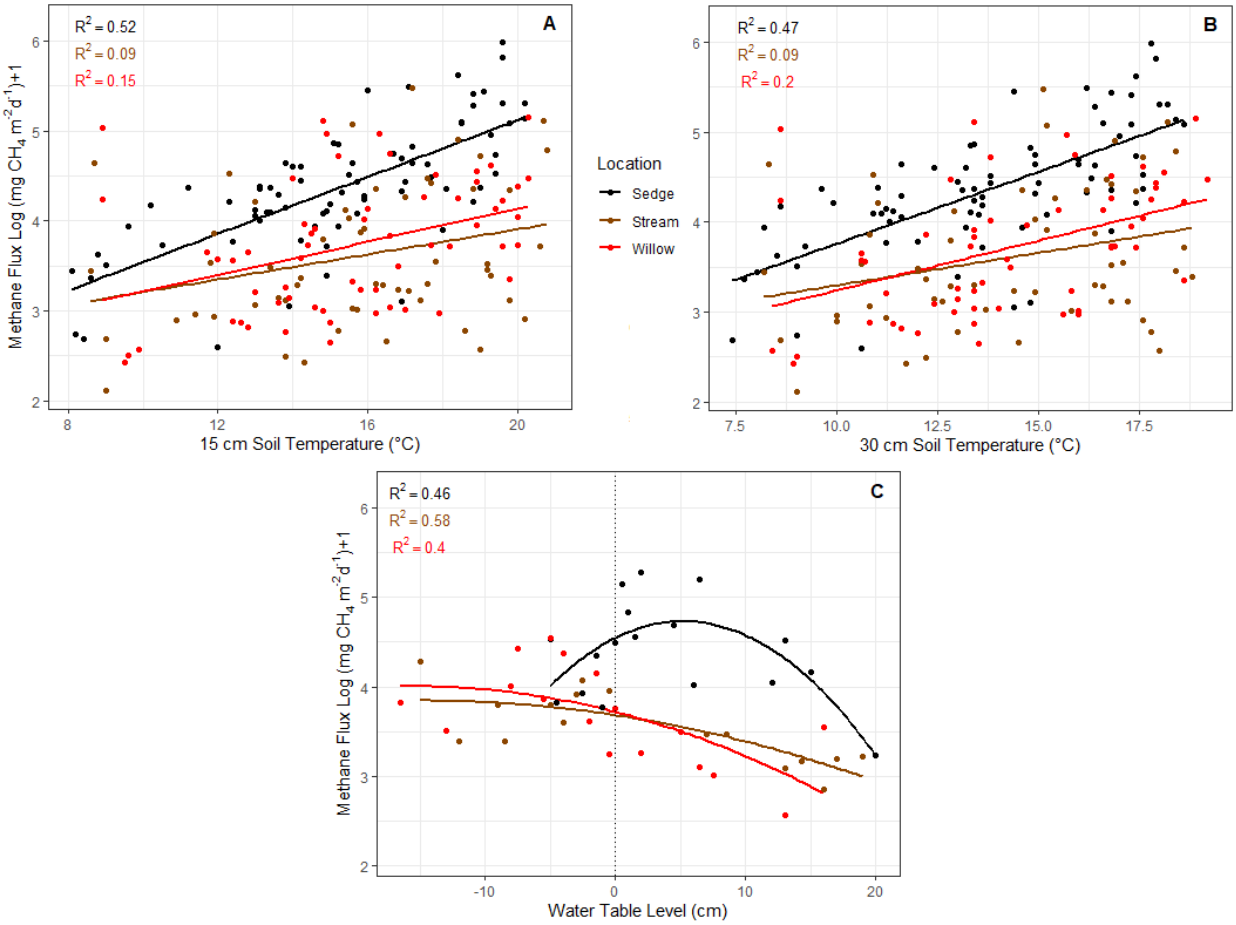

Figure 3.6: Scatterplots that show the relationships between log CH_4 fluxes and soil temperature at 15 and 30 cm as well as water table level (cm). Each graph was separated by defined study areas. Positive trends are present for both soil temperature depths while a unimodal relationship exists for water table.

3.3.3.4 Controls on Methane Fluxes

The significant variables that explained variation of steady CH_4 fluxes that were included in the LME model differed among locations (Table 3.5). Water table was the only environmental factor that was a significant predictor at all sites, as well as for the overall model. While soil temperature at 15 cm was significantly related to steady CH_4 fluxes for the overall model, it was only found to be significant within the sedge location. Furthermore, the interaction between water table and soil temperature at 15 cm was considered significant at the sedge location. This interaction was significant and occurred as warmer soil temperatures increased CH_4 emissions at a greater rate when the water table was near the surface. Pore water CH_4 concentration at 40 cm was only considered significant at the willow location where the interaction between water table and pore water was also significant. Generally, as pore water CH_4 concentrations increased in this location, so did CH_4 fluxes. The interaction between water table and pore water CH_4 concentration was found to be significant possibly due to pore water CH_4 concentrations

being their greatest during optimum water table levels for CH_4 fluxes. For the overall model, pore water CH_4 concentration at 40 cm, the interaction between water table and soil temperature at 15 cm as well as the interaction between soil temperature at 15 cm and pore water CH_4 concentration at 40 cm were found to be significant factors in explaining variation in CH_4 fluxes in addition to water table and soil temperature at 15 cm. Pore water CH_4 concentration at 40 cm was a significant fixed factor as greater pore water concentrations typically resulted in greater steady CH_4 fluxes. As for the interaction between soil temperature and pore water concentration at 40 cm, an increase in soil temperatures can lead to an increase in pore water CH_4 concentrations due to enhanced microbial activity. Finally, the interaction between water table and soil temperature at 15 cm highlights the fact that the relationship between CH_4 production and temperature is often dependant on water table levels.

Table 3.5: Statistical results of each linear mixed effects model. Variables that were included in the initial models were soil temperature at 15 and 30 cm, water table level, GEP, pore water CH_4 concentration at 15 and 40 cm as well as two-way interactions between each singular variable.

Model	Variable	F	*p*	R^2m	R^2c
Sedge	Water table	$F_{1,71} = 5.2$	**0.0258**	31.0	38.3
	Soil Temperature 15 cm	$F_{1,71} = 27.3$	**<0.0001**		
	Water Table x Soil Temperature 15 cm	$F_{1,71} = 6.0$	**0.0170**		
Stream	Water table	$F_{1,55} = 4.1$	**0.0485**	5.0	29.6
Willow	Water table	$F_{1,66} = 4.6$	**0.0356**	11.5	12.5
	Pore water CH_4 concentration 40 cm	$F_{1,66} = 5.2$	**0.0257**		
	Water table x Pore water CH_4 concentration 40 cm	$F_{1,66} = 5.3$	**0.0242**		
All	Water table	$F_{1,194} = 19.6$	**<0.0001**	22.3	59.8
	Soil Temperature 15 cm	$F_{1,194} = 61.8$	**<0.0001**		
	Pore water CH_4 concentration 40 cm	$F_{1,194} = 4.0$	**0.0466**		
	Water table x Soil Temperature 15 cm	$F_{1,194} = 4.8$	**0.0296**		
	Soil Temperature 15 cm x Pore water CH_4 concentration 40 cm	$F_{1,194} = 8.9$	**0.0033**		

3.4 Discussion

3.4.1 Long-term Growing Season Methane Trends and Predictors

Over the course of four years of sampling, average growing season steady fluxes ranged from 28.5 mg CH_4 m^{-2} d^{-1} to as high as 202.7 mg CH_4 m^{-2} d^{-1}. Only two years, 2016 and 2019, were found not to have significant differences between CH_4 fluxes. This multi-year set of data helps demonstrate the complexity, as well as the ebbs and flows, that a peatland can go through in terms of CH_4 fluxes on an

annual basis. The amount of CH_4 emitted from a peatland is not likely to be consistent year to year (Turetsky et al., 2008). It is possible, in some instances such as this study, where there appears to be an anomaly year where CH_4 fluxes were over 2.5 times greater than every other year. Likewise, the same can occur in terms of abnormally low CH_4 fluxes. In 2018, the average steady CH_4 flux was nearly half of the second lowest yearly flux. This is important to consider and keep in mind during peatland management or estimates of global CH_4 emissions. If certain predictions are made based on a single growing season, it is possible that the single year of measurements could be an over- or underestimation of the average CH_4 fluxes that occur on a longer trend (Moore et al., 2011; Bieniada et al., 2020). It is important to use several years of data when possible to improve the reliability of total CH_4 flux estimates, as well as to evaluate how a peatland reacts to changes in environmental conditions over time.

The main reason why these large discrepancies exist in CH_4 fluxes year to year in this fen is likely due to a difference in water table levels over the course of the growing season. The year 2017 had a significantly higher water table than every other year. The average water table level in 2017 was 8.2 cm, which was 4.8 cm greater than the second highest average water table and 15.2 cm greater than the lowest average water table. Flux measurements rarely took place when the water table was below the surface in 2017 while that was a common occurrence during the other years. This meant that over the course of the growing season, the entire peat column was maintained under saturated conditions, limiting the amount of available oxygen found within the peat (Blodau and Moore, 2003). While complete saturation of peat is typically ideal for CH_4 fluxes, standing surface water can create an oxygenated water column that can lead to an enhancement of CH_4 oxidation (Bubier et al., 1995). However, a synthesis analysis of 71 wetlands that was completed by Turestky et al. (2014) found that the optimum water table position for CH_4 flux in rich fens is above the surface. Rich fens, such as this one, likely maintain high CH_4 flux even in the presence of an oxygenated water column due to the aerenchyma that is present in the vascular vegetation typically found within these ecosystems. Vascular plants in these locations develop porous tissue that is used to transport oxygen to other areas of the plant that are submerged in water; however, these pathways can also be used to transport CH_4 from the peat to the atmosphere and bypass oxidation (Joabsson et al., 1999).

Over the course of larger time scales, such as an entire growing season, water table appears to be an ideal predictor of mean steady CH_4 flux. Similar trends have been found in other studies such as Turetsky et al., (2008) when they viewed a decrease in overall CH_4 fluxes in 2006 from 2005 due to a

drier year with a reduced water table. Likewise, in an Albertan bog, Munir and Strack (2014) attributed reductions in CH_4 between years to a drier growing season which resulted in lower water table levels. These long-term trends are especially important when modelling peatlands' responses to future climate scenarios caused by climate change. Peatlands, especially rich fens, that reside in areas that will experience an increase in precipitation over the course of the growing season due to climate change will likely see an increase in overall CH_4 emissions due to a reduction in the size of the oxic zone. Meanwhile, the opposite will likely occur in peatlands that may receive less precipitation or lowered water table due to increases in evapotranspiration under warmer air temperature that exceed summer precipitation increases.

When examining steady CH_4 fluxes on a shorter time period such as monthly, temperature appears to be a superior indicator than water table. For every year except for 2016, mean steady CH_4 fluxes were the greatest in either July or August, which is when the warmest soil temperatures were recorded. Positive correlations between soil temperature and CH_4 fluxes have also been shown for the year 2019 (Figure 3.6). Pugh et al. (2018) found similar results in a Wisconsin shrub fen as CH_4 fluxes had a strong temperature response when examined on a monthly timescale. Additionally, Treat et al. (2007) identified that mean air temperature and water table depth were the strongest predictors of CH_4 fluxes in a temperate fen. Likewise, on a multi-year record of CH_4 fluxes from a southern Canadian bog, temperature was considered to be the dominant correlation (Moore et al., 2011). These results support the concept that increasing temperature leads to an increase in microbial activity (Chowdhury et al., 2013), which often leads to an overall increase in CH_4 production and emissions. Increasing soil temperatures can also lead to an increase in plant productivity and the supply of substrates and additional labile carbon that is required in the production of CH_4 (Joabsson et al., 1999; Pelletier et al., 2007). Water table also plays an important role for temperature response. If the conditions of a peatland are wet and ideal for CH_4 production and emissions, the temperature flux relationship will be much stronger than when dry (Munir and Strack 2014). This is because under dry conditions, despite temperatures being warm and idea for CH_4 production, oxidation of CH_4 will occur at a much faster rate. This has been highlighted in the LME model that found significant interactions between temperature and water table, as well as the steeper slope for temperature-CH_4 flux relationship at the sedge site (Figure 3.6) as that area was consistently wetter than the other two.

When assessing or predicting CH_4 fluxes from a single peatland, water table and soil temperature appear to be the best predictors. For this fen in particular, water table is an excellent

predictor of CH_4 fluxes on a longer temporal scale, such as across the entire growing season, while soil temperature acts as a better predictor on a monthly scale. While this is true for this fen, it may not always be the case. During a 5-year analysis of CH_4 fluxes from Sallie's Fen, Treat et al. (2007) determined that mean seasonal CH_4 flux was best predicted by air temperature while water table was found to not improve their overall model. Differences in findings can likely be explained by the inclusion of episodic ebullition at Sallie's fen that produced some of the highest overall CH_4 fluxes and occurred at low water table levels, leading to a poor correlation between CH_4 flux and water table (Treat et al., 2007). Issues such as this did not arise in this study as episodic ebullition was removed from steady flux measurements.

3.4.2 Spatial Comparison of Methane Fluxes and Environmental Controls

In terms of average steady CH_4 flux, fluxes were over two times greater in the sedge area than both the stream and willow area. This discrepancy shows that spatial variability of CH_4 fluxes exists throughout the fen. The willow collars were initially installed to determine if the presence of *Salix* influenced CH_4 fluxes in any way. While some studies have shown that trees can emit CH_4, thereby increasing total peatland emissions (Gauci et al., 2010; Pangala et al., 2013), knowledge of how woody plant materials transport CH_4 from the soil into the atmosphere and the potential for oxidation within stems and branches remain uncertain (Covey et al., 2019). Although a past study found that *Salix* species enhanced the overall release of CH_4 compared to *Juncus* (Smialek et al., 2006), it appears unlikely that *Salix* were able to enhance CH_4 fluxes more than *Carex* in this fen. Both the sedge and stream locations, which contained no *Salix,* had greater average CH_4 fluxes than willow plots. While the willow location did have the lowest CH_4 fluxes, this result is likely explained by other environmental factors rather than the presence of *Salix*.

Over the course of the growing season, water table was the lowest in the willow area. Average water table levels were above the surface for the sedge and stream locations but the same could not be said for the willow location. Having the lowest water table meant that potential for oxidation would be at its greatest in this location of the fen. Despite average water table levels differing only 2 cm in the sedge and stream location, fluxes were still over two times greater in the sedge location. Insight into this spatial variability can be gained from pore water CH_4 concentrations at 15 cm that were four times greater in the sedge location than at the stream. One explanation for the stream location having such low pore water CH_4 concentrations could be due to its proximity to the tributary stream. Free flowing surface water can carry water that is rich in oxygen and can mix with subsurface water found in the

peat. This can lead to increasing oxygen levels in the peat that can subsequently reduce CH_4 production and lead to an increasing rate of oxidation (Freeman et al., 1996) and reduction in pore water CH_4 concentration. Another possible explanation for the stream and willow locations having much smaller CH_4 fluxes than the sedge location is due to a difference in water chemistry. The hydrologic gradient of the fen appears to differ between the sedge area and the stream and willow locations. A difference in hydrologic gradient and hydrologic flow can result in a difference in water chemistry. If more favourable terminal electron acceptors such as sulfate and nitrate were present in the stream and willow area of the fen, this would also result in a reduction in CH_4 production and a promotion of organic matter mineralization in the anoxic zones (Smemo & Yavitt, 2011). Future research at this fen should measure oxygen content and concentrations of inorganic terminal electron acceptors across the different areas to better understand how local hydrology affect CH_4 cycling.

Despite differences in the strength of relationships between soil temperature and steady CH_4 fluxes amongst location, soil temperature along with water table levels have been shown to be important factors in explaining the variance of CH_4 fluxes within this fen. While GEP has been demonstrated to have a relationship with CH_4 fluxes in past studies (Waddington and Roulet, 1996; Waddington and Day 2007), no significant relationship was found in any of the models that were constructed. This is possibly explained by the willow collars having much higher GEP than the sedge and stream area which would lead to a poor correlation between CH_4 fluxes and GEP. Additionally, GEP may not have been significant at each grouping due to a lack of variability of GEP between collars. These findings further shine light on the heterogeneity that exists within peatlands. It has been demonstrated that spatially, significant environmental controls of CH_4 will vary.

3.4.3 Non-growing Season Methane Fluxes

Over the course of the growing season, varying amounts of CH_4 were released from the fen through steady fluxes. The amount of CH_4 that was released from the years 2016-2019 were 9.4, 30.6, 4.2 and 11.7 g CH_4 m^{-2}, respectively. These differences highlight the amount of variability that can occur within a peatland on a year to year basis. The greatest amount of CH_4 that was released in a single year was over seven times greater than the year with the lowest of CH_4 emissions. When looking at CH_4 released in the non-growing season (October 1st – December 31st), there is much less variability with 2.4, 2.4, 1.7 and 2.6 g CH_4 m^{-2} of CH_4 being released during this time period for the years 2016-2019, respectively. Despite the 2017 growing season releasing CH_4 at a rate that was several times greater than every other year, a different trend emerges for the non-growing season. With the exception of the

year 2018, non-growing season CH_4 emissions were extremely similar to one another even though that was not portrayed in the growing season. It is important to remember that these values are based on only steady CH_4 fluxes and ignore the contribution of ebullition. From Chapter 2, it has been shown that ebullition can contribute a substantial amount of CH_4, especially in the growing season. While ebullition was measured during one of the non-growing season months (October), it was apparent that ebullition at this time was quickly declining and occurred at a much higher rate in the growing season. This indicates that when accounting for ebullition, growing season emissions would increase at a greater magnitude than the non-growing season, leaving the non-growing season representing a lower percentage of the growing season emissions than previously calculated.

Currently, omitted flux rates from the non-growing season are typically calculated by assuming that the non-growing season is equal to 15% of the growing season (Webster et al., 2018). However, results from this study show that a relationship between the two seasons likely does not exist, and that they should be treated, and calculated, separately. An abnormally high CH_4 release in the growing season in 2017 did not result in an abnormally high non-growing season emission. In terms of percentage of growing season, despite only having measurements for under half of the non-growing season, the years 2016, 2018 and 2019 have all surpassed 15% of growing season steady CH_4 flux emissions. The non-growing season already represents 25.7, 41.0 and 21.6% of the total growing season emissions for these years, respectively, while the 2017 non-growing season is a much smaller proportion of growing season fluxes equalling only 7.8% of the growing season, largely due to the very high growing season emissions in that year. While January and February would likely not contribute a substantial amount of CH_4, March and April could when temperature begins to rise and ice begins to melt (GaŽovic et al., 2010). Based on this extrapolation of the measured September – December season fluxes to the whole non-growing season for 2019, as well as incorporating the contribution of ebullition (Chapter 2) and the additional collars, the non-growing season fluxes at this site accounted for 25.0% of annual emissions and were equal to 33.3% of the growing season value.

Comparing these findings to other studies is difficult as not many studies have focused on non-growing season CH_4 emissions, and when they have, growing season length is often not defined or is much longer than the criteria used for this study. Additionally, total measurements during the non-growing season are infrequent and likely do not give an accurate representation of what is truly occurring. A study done in a boreal peat bog in West Siberia found that 'cold season' CH_4 fluxes only contributed 3.5 to 11% of annual emissions (Panikov and Dedysh, 2000). However, issues arise as their

'cold season' (September to May) emissions were calculated by simply taking measurements in February and assuming that they were an acceptable representation for the entirety of the non-growing season. It is not a surprise that the contribution of CH_4 for the 'cold season' was so minimal when measurements from one of the coldest months of the year were assumed to be the same for the months shouldering the growing season. Similarly, when Pelletier et al. (2007) determined that winter contributed 13% of overall annual emissions, the result was based on measurements taken in only November and March. It is difficult to gain a true representation of the contribution of winter emission when there are only measurements for 2 out of 7 months. Median non-growing season emissions for all wetlands at midlatitudes (40°-60 °N) based on a synthesis of available data was found to be 16.0% (95% CI: 11.0%-23.0%) of annual emissions (Treat et al., 2018), which is lower than what was found for the entirety of 2019 in the present study. While Strack et al. (2004) found winter fluxes of up to 23.8% of annual emissions in a Quebec fen, their defined growing season was much longer than the one used in this study which can severely reduce the amount of non-growing season emissions. For Strack et al. (2004), their growing season was a total of 199 days while the growing season for this study was only 152 days. If Strack et al. (2004) used the same growing period as this study, it is likely that their non-growing season fluxes would surpass 30% of annual emissions. However, one study done in a boreal mire in Finland (Leppälä et al., 2011) followed very similar criteria and sampling procedures to the present study. Their non-growing season was defined as 6 months, and sampling occurred one time each month during this period in five various sites. Two sites had non-growing season CH_4 emissions equal 26 and 28% of annual emissions. Furthermore, an additional site had non-growing season emissions contribute 38% of annual emissions. These findings are quite similar to what was found in the present study, and also demonstrate that non-growing season emissions can represent up to nearly 40% of annual emissions.

To this day, our understanding of non-growing season CH_4 fluxes remains very limited. Research that has been completed is often lacking a sufficient number of measurements to accurately portray the true amount of CH_4 release during this time period. Issues also arise when defining the growing season and non-growing season. Studies that use a much longer growing season, including sites where the growing season does represent a much larger proportion of the year, in comparison to this study will likely have a much smaller percentage of contribution from the non-growing season. Additional research is required throughout the entirety of the non-growing season in peatlands to gain a greater understanding of how CH_4 fluxes during this period compare to the growing season. It is especially important in more northern latitudes as the non-growing season tends to make up the majority of the

year. Eddy covariance towers are becoming more common for measuring CH_4 emissions and could be an ideal way to obtain measurements during the non-growing season (Knox et al., 2019). However, issues still arise with this technique due to high power requirements of CH_4 sensors making them difficult to run over the winter in remote locations. Using a baseline of the non-growing season equaling 15% of the growing season or annual emissions appears to be inaccurate and the contribution of the non-growing season appears to be much greater than that in certain geographic areas. Using this technique can lead to a substantial underestimation of annual CH_4 emissions from specific peatlands, as well as the entire global CH_4 budget.

3.5 Conclusion

Methane fluxes were highly variable interannually and appeared to be dependent on water table levels for the growing season. Higher average water table levels during the growing season resulted in greater steady CH_4 fluxes. While water table appears to be an ideal indicator of steady CH_4 fluxes on the growing season scale, soil temperature was a better indicator on a monthly scale. CH_4 fluxes were also found to vary spatially throughout the fen in 2019 as fluxes were over two times greater in the sedge location. This was likely due in part of the sedge location consistently having a higher water table than the other locations. Despite research suggesting that trees or woody plants can enhance CH_4 fluxes, the presence of *Salix* did not influence CH_4 fluxes in any noticeable way. Non-growing season CH_4 emissions were considerably greater than the suggested 15% of the growing season in three of the four years. Furthermore, three of the four non-growing seasons had nearly identical emission totals which could suggest that non-growing season emissions typically fall within a stable range that is not greatly influenced by the growing season conditions. This suggests that there is no consistent relationship between the two seasons, and each should be measured and investigated separately especially in more northern peatlands where the non-growing season tends to be much longer. While it is difficult to measure CH_4 fluxes in the non-growing season, it is vital to expand our understanding of this lengthy time period and to generate accurate annual emission estimates. With the majority of peatlands residing in the boreal region (Joosten and Clarke, 2002), it is possible that annual CH_4 emissions are being underestimated due to consistently underestimating the amount of CH_4 that is being emitted during the non-growing season. Additionally, having a standard way of defining the growing season would lead to a more ideal approach when comparing non-growing season emissions between studies and sites.

Chapter 4: Summary and Conclusions

Results of this study have highlighted the spatiotemporal variability and magnitude of CH_4 dynamics within a calcareous fen peatland. Ebullition was measured across the growing season in 2019 which revealed some interesting relationships. Ebullition was shown to vary significantly on both a spatial and temporal scale. From May up until August, ebullition increased not only in volume but overall emissions as well. Additionally, the three centralized locations where the funnel traps were placed highlighted how differences in peat properties and hydrology can greatly impact ebullition rates. Our models showed that soil temperature and pore water CH_4 concentrations can explain a great deal of variation in ebullition. Additionally, precipitation was shown to typically reduce ebullition initially by increasing water table levels and hydrostatic pressure. A greenhouse experiment determined that increases in vascular plant coverage can lead to a decline in pore water CH_4 concentration likely due to increases in oxidation and consistent plant mediated transport of CH_4 and that this reduces ebullition significantly. While a lot was learned from this study, future research is still needed to diminish the knowledge gap on peatland ebullition. Overall, ebullition needs to be measured more frequently throughout all peatlands to more accurately determine the amount of ongoing CH_4 emissions attributed to this process, as it has been shown to contribute a meaningful amount. Furthermore, additional experiments can be conducted with a series of cores or field plots that represents a gradient of sedge cover to investigate at which point plant cover starts to reduce ebullition flux. Also, there remains a knowledge gap for how non-vascular vegetation such as mosses influences ebullition.

Similar to ebullition, steady CH_4 fluxes were found to be variable both spatially and temporally. Average flux rates varied across a four-year period. For longer timescales such as the growing season, water table appeared to be an ideal predictor of steady CH_4 fluxes, while temperature was a more suitable predictor for monthly timescales. In the growing season of 2019, the sedge area had the highest CH_4 emissions likely due to high water table levels and pore water CH_4 concentrations that were likely influenced by the hydrologic gradients throughout the fen. Non-growing season steady CH_4 emissions were shown to be greater than 15% of the growing season in three of the four years. This highlights the importance of measuring non-growing season fluxes for more accurate modeling and estimates of CH_4 emissions. Initially, it was planned to continue measuring non-growing season steady CH_4 fluxes throughout the entirety of 2019, up until April 2020. However, this was not able to be completed due to the COVID-19 outbreak. Due to this, assumptions had to be made to determine the contribution of the entire non-growing season for the year 2019/2020. This research has helped identify the importance of

non-growing season CH_4 emissions. There should be an increased effort of obtaining non-growing season emissions data throughout all peatlands. Doing so will lead to more accurate global CH_4 estimations, as well as modelling. Furthermore, for peatland management practices, it is important to have as much accurate information as possible available for decision making. Knowledge of relationships between non-growing season CH_4 emissions and environmental variables remains poor. The influence of ice and snow cover above the peat likely influences CH_4 emissions in some capacity, but additional research is needed to quantify these relationships. Furthermore, the growing season and non-growing season need to be more consistently defined and justified in studies. The lengths of these two seasons can drastically influence results and overall emissions rates.

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